THE UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR . Nejla H. Senturk . . . .

TITLE OF THESIS . THE VAPOR PRESSURE, CRITICAL PROPERTIES . . .

REFRACTIVE INDICES AND VOLUMETRIC BEHAVIOR

OF CARBONYL SULFIDE . . . .

DEGREE FOR WHICH THESIS WAS PRESENTED . . . M. Sc. . . . . . .

YEAR THIS DEGREE GRANTED . . . . 1977 . . . .

Permission is hereby granted to THE UNIVERSITY
OF ALBERTA LIBRARY to reproduce single copies of this thesis
and to lend or sell such copies for private, scholarly or
scientific research purposes only.

The author reserves other publication rights, and
neither the thesis nor extensive extracts from it may be
printed or otherwise reproduced without the author's written
permission.

THE UNIVERSITY OF ALBERTA

THE VAPOR PRESSURE, CRITICAL PROPERTIES, REFRACTIVE INDICES,

AND VOLUMETRIC BEHAVIOR OF CARBONYL SULFIDE

by

© NEJLA H. SENTURK

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE IN CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

EDMONTON, ALBERTA

FALL, 1977

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies and
Research, for acceptance, a thesis entitled "THE VAPOR
PRESSURE, CRITICAL PROPERTIES, REFRACTIVE INDICES, AND
VOLUMETRIC BEHAVIOR OF CARBONYL SULFIDE" submitted by
NEJLA HALIME SENTURK in partial fulfilment of the
requirements for the degree of Master of Science in
Chemical Engineering.

To My Husband

YASIN

ABSTRACT

Experimental volumetric data for carbonyl sulfide along
the 273.2 and 323.2 isotherms and the 383.2 K isotherm were obtained
by using a Burnett apparatus at pressures up to the vapor pressure
of carbonyl sulfide and to about 49 700 kPa, respectively. These
observed data were used to calculate compressibility factors for
carbonyl sulfide.

Using a high-pressure constant-volume windowed liquid-
level gauge, vapor pressure data for carbonyl sulfide were observed
at temperatures ranging from 264.5 K to the critical point. The
critical temperature, pressure, and volume of carbonyl sulfide were
determined to be 378.8 K, 6349 kPa, and 0.135 m^3/kmol respectively.
These values were compared to earlier values reported in the
literature. The critical temperature agreed within 0.6 K of three
earlier measurements, the critical pressure agreed within 35 kPa of
the only other previously measured value, and the critical volume was
within 0.001 m^3/kmol of the average of two earlier estimated values.

The refractive indices of carbonyl sulfide along the 273.2,
288.2, 303.2, 323.2, 343.2, 363.2, and 383.2 K isotherms were
obtained using a helium - neon laser and an autocollimating
telescope mounted on a windowed cell at pressures ranging from the
vapor pressure to approximately 20 700 kPa. These experimentally
observed data were used in the Lorentz-Lorenz molar refractivity
relationship to calculate the densities of carbonyl sulfide.

Finally, using the pertinent experimental data as input to
a typical multiconstant equation of state (the Benedict-Webb-Rubin)

and a typical cubic equation of state (the Peng-Robinson) the molar volumes, compressibility factors, and vapor pressure of carbonyl sulfide were predicted. The results compare favorably with the experimental data obtained in this study.

ACKNOWLEDGEMENTS

vii

The author wishes to express her sincere gratitude and appreciation to the following persons and organizations:

Dr. D. B. Robinson, for his advice, encouragement, and especially for his guidance in the supervision of this investigation,

Dr. H. Kalra, Dr. H. J. Ng, Dr. D.Y. Peng and N. P. Freitag, for their valuable suggestions and help with the problems associated with this thesis,

Dr. Y. Chu, for translating the German articles,

Mr. H. Rempis, for his help during the experimental study especially on the variable volume vapor-liquid equilibrium cell,

The personnel of the machine and instrument shops of the Department of Chemical Engineering, for their assistance and cooperation,

Mrs. A. Mayes for typing the manuscript,

The University of Alberta, the National Research Council of Canada and the Research Council of Alberta, for their financial support,

Her husband, Yasin, for his understanding and continued encouragement made completion of this study possible.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I - INTRODUCTION

In general, petroleum reservoir fluids contain both a wide range of hydrocarbons and several non-hydrocarbons such as nitrogen, hydrogen sulfide, carbon dioxide and helium in their original state. Although other sulfur compounds such as carbonyl sulfide and carbon disulfide do not usually occur in virgin petroleum fractions, they may be formed during thermal or catalytic processing operations. For example, carbonyl sulfide is formed during the process of manufacturing sulfur from hydrogen sulfide in the presence of carbon dioxide and methane which are both present in typical sulfur recovery plants. Furthermore, carbonyl sulfide may also be formed during the manufacture of substitute natural gas from coal which contains carbon, oxygen and sulfur.

Recent trends toward improved environmental protection require a more complete removal of sulfur compounds from the plant effluent than was common in earlier times. Furthermore, more stringent specifications on refined products such as propane and butane make it necessary to design better processes in order to remove and dispose of these harmful sulfur compounds safely and efficiently.

However, the design of plants and sound processes for separating carbonyl sulfide from the associate compounds require a knowledge of the physical and thermodynamic properties of carbonyl sulfide. Although a limited amount of information on the behavior of carbonyl sulfide has been obtained previously, most of the data has been obtained by Kemp and Giauque (1) along the vapor pressure curve in a temperature range from 161.8 to 223.8 K. No previous single phase volumetric data could be found, although Partington and Neville (2)

measured equilibrium liquid and vapor densities of carbonyl sulfide from 303.2 K to near the critical point. Also there is only one vapor density measurement for carbonyl sulfide at 298.2 K and atmospheric pressure by Kemp and Giauque (1).

Attempts have been made to determine the critical properties but currently there is a significant difference in the reported values of the critical temperature from 375.4 to 409.1 K, and the critical pressure from 6181.6 to 8319.1 kPa. No previous attempts have been made to determine the critical volume of carbonyl sulfide.

Consequently, it has been decided that it would be worthwhile to:

1. Determine volumetric data in the single-phase region at 273.2 and 323.2 K at pressures below the vapor pressure and at 383.2 K at pressures to 49 700 kPa.

2. Determine experimentally the vapor pressures at temperatures ranging from about T_R = 0.7 to the critical point and hence simultaneously determine the critical properties T_c, P_c, V_c, and the acentric factor ω.

3. Determine the refractive index of pure carbonyl sulfide at seven different temperatures from 273.2 to 383.2 K pressures ranging from the vapor pressure to about 20 700 kPa.

4. Determine the Lorentz-Lorenz refractivity of pure carbonyl sulfide using the density and refractive index data obtained in (1) and (3) above.

5. Calculate the density of carbonyl sulfide at each of the seven temperatures referred to in (3) above over the experimental pressure range.

II - LITERATURE REVIEW

The existence of carbonyl sulfide was not confirmed until 1867 when it was prepared by Than (3) using the reaction of carbon monoxide with sulfur vapors. Since then, it has been prepared by other investigators in a variety of ways. A comprehensive review of these methods and the chemistry involved have been presented by Ferm (4). In addition, some of the earlier studies on the properties of carbonyl sulfide (COS) have been discussed in detail by Miranda (5). However, the more pertinent of these will be reviewed again here.

A. Volumetric Properties

As mentioned previously, no volumetric data on the behavior of carbonyl sulfide in the single phase fluid region have been published. However, Partington and Neville (2) have reported the liquid density of carbonyl sulfide between 173.2 K and 372.2 K. They expressed the results of their measurements by the following empirical equation:

$$\rho_1 = 1.049 - 0.0029t - 6.76 \times 10^{-6} \, t^2 \tag{1}$$

where t is in °C and this equation represents the experimental results from 173.2 to 323.2 K. In addition, Partington and Neville determined the equilibrium liquid and vapor densities of carbonyl sulfide from 303.2 K to near the critical point. Stock and Kuss (6) reported the density of liquid carbonyl sulfide at 186.2 K to be 1.24 g/ml. Pearson, Robinson, and Trotter (7) measured the density of liquid carbonyl sulfide at three temperatures and obtained 1.073 g/l at 273.2 K, 1.028 g/ml at 290.2 K, and 0.986 g/ml at 305.4 K. These values are all about three percent higher than those calculated by Equation (1) proposed by Partington and Neville. Kemp and Giauque (1) reported the

vapor density of carbonyl sulfide to be 2.4849 g/l at 298.2 K and atmospheric pressure. This is the only vapor density measurement reported for carbonyl sulfide.

B. Vapor Pressure and Critical Properties

B-1. Vapor Pressure

The vapor pressure of carbonyl sulfide was studied by Hempel (8), Ilosvay (9) and, Stock and Kuss (6) for a limited number of temperatures. The vapor pressure of carbonyl sulfide in a temperature range from 161.8 to 223.8 K was measured by Kemp and Giauque (1). The data were fitted to the following equation: -

$$\log_{10}(P) = - (1318.260/T) + 10.15309 - 0.0147784T$$
$$+ 0.000018838T^2 \tag{2}$$

where P is the absolute pressure in cm.Hg., and T is the absolute temperature in K. Later, Honig and Hook (10) used an equation of the form

$$\log_{10}(P) = AT^{-1} + B \log_{10}T + CT + DT^2 + E \tag{3}$$

to fit Kemp and Giauque's vapor pressure of carbonyl sulfide observations but they did not report the values they obtained for A, B, C, D, and E. The Matheson Gas Products Company (11) has presented the vapor pressure of carbonyl sulfide graphically between the boiling point and the critical point. An equation developed by Kemp and Giauque (1) could have been used for obtaining the values at temperatures below 223.8 K, but no explanation is given on the method used for higher temperatures. Recently, the vapor pressure of carbonyl sulfide was determined by Miranda (5) at temperatures from 266.2 K to near the critical point.

B-2. Critical Properties

The critical temperature and pressure of carbonyl sulfide were first determined to be 378.2 K (105°C) and 6384 kPa (63 kg/cm^2), respectively by Hempel (8). Also, the critical temperature of carbonyl sulfide was measured as 378.2 K (105°C) by Ilosvay (9), but Hempel and Ilosvay did not report the details of their measurements. Partington and Neville (2) determined the critical temperature of carbonyl sulfide by observing the disappearance of the two phase meniscus at 375.4 K (102.2°C). Kobe and Lynn (12) estimated the critical pressure of carbonyl sulfide to be 6181 kPa (61 atm) by using the vapor pressure data of Stock and Kuss. However Lydersen (13) estimated the critical pressure of carbonyl sulfide to be 6586 kPa (65 atm). Finally, Miranda (5) obtained estimates of the critical temperature and pressure by extrapolating the experimental refractive index measurements. The values he obtained were 386.2 K (235°F) and 6619 kPa (960 psia), respectively. The critical volume of carbonyl sulfide has not been determined previously, but it was estimated to be 134 ml/mol by Lydersen (13) and 138 ml/mol by Kobe and Lynn (12).

C. Refractive Index

Refractive index measurements are useful for calculating the densities of pure compounds and mixtures, because for a given substance the refractive index is related to the density, and is given by the Lorentz-Lorenz equation below:

$$R_{LL} = \frac{1}{\rho} \cdot \frac{n^2-1}{n^2+2} \tag{4}$$

where ρ is the density, n is the refractive index, and R_{LL} is the molar refractivity.

Francis (14) measured the refractive index of liquid carbonyl sulfide in the temperature range from 265.0 to 299.9 K. Wong and Anderson (15) also measured the refractive index of liquid carbonyl sulfide at 186.15 K and reported the molar refractivity to be 11.29 ml/mol. More recently, Miranda (5) determined the refractive index of carbonyl sulfide at 293.2, 333.2, 373.2, 413, and 453 K with pressures ranging from saturation pressure of carbonyl sulfide up to about 6895 kPa, but did not report his calculated refractivity values.

D. Other Properties

Since carbonyl sulfide occurs as a contaminant in many refinery gases, its corrosive properties are of interest. Nelson, Veal, and Heinrich (16) verified that carbonyl sulfide does not produce a tarnished strip in their copper corrosion test. Except for these findings, information is not available on the action of carbonyl sulfide towards other metals. Freise (17) discovered that carbonyl sulfide is corrosive toward concrete.

Cross (18) and Kemp and Giauque (1) determined the melting point, boiling point, heat capacities, and heats of fusion and vapor-ization of carbonyl sulfide. More recently, McBride and Gordon (20) used spectroscopic data to calculate the thermodynamic functions of carbonyl sulfide in the ideal gas state. Zandler, Watson, and Eyring (21) applied significant structure theory to calculate the thermodynamic properties of carbonyl sulfide in the liquid region. As far as can be ascertained, the thermodynamic properties of carbonyl sulfide such as enthalpy, entropy, and density have so far never been calculated as a function of pressure and temperature.

E. A General Statement

.Each of the aforementioned measurements require the use of different experimental apparatus and procedures. In each case, existing equipment together with appropriate modifications was used whenever required. The volume measurements on a standard Burnett apparatus and the vapor pressure and critical properties in an existing high pressure windowed liquid level gauge were carried out. The refractive index measurements were obtained by using an existing variable volume vapor-liquid equilibrium cell equipped with a special mirror and window arrangement and an autocollimating telescope.

Since there are significant differences in both the method and the procedures of these measurements, it is considered advantageous to deal with each set of measurements separately in the following sections.

III - VOLUMETRIC PROPERTIES

A. Experimental Method

The experimental method used in this work was based on that proposed in 1936 by Burnett (22). Because of its basic simplicity, the Burnett method has been used in recent years by many investigators to study the volumetric properties of gases over a wide range of temperature and pressure. This technique requires the measurement of only temperature and pressure on successive isothermal expansions of a gas, and does not require a knowledge of the mass of gas charged to the system. This is an advantage, since temperature and pressure can be measured with high precision and accuracy, while the accurate determination of the system volume and the mass of a gas sample are relatively more difficult.

The Burnett apparatus consists of two vessels of constant unspecified volume connected to each other by means of an expansion valve. Initially, the first vessel is filled to the desired initial pressure with the gas to be studied. Temperature is maintained at a constant value and the pressure is measured. The gas is expanded into the evacuated second vessel, and the pressure is measured after thermal equilibrium has been established. The expansion valve is closed, and the second vessel is again evacuated. This sequence is repeated so that a series of pressures $P_o, P_1, \ldots\ldots, P_{j-1}, P_j$ is obtained for each experimental run at the chosen temperature.

The details of this procedure and the derivation of the equations necessary for determining compressibility factor at each pressure have been presented by other workers (22, 23, 24, 25, 26). For convenience, some of the pertinent relationships are given here.

If V_1 and V_2 represent the volumes of vessels 1 and 2, the states of the gas prior to and after the jth expansion are given by:

$$P_{j-1} \, (V_1)_{j-1} = Z_{j-1} \cdot n_{j-1} \cdot R \cdot T_{j-1} \tag{5}$$

$$P_j \, (V_1 + V_2)_j = Z_j \cdot n_j \cdot R \cdot T_j \tag{6}$$

Since vessel 2 is evacuated prior to the jth expansion, $n_{j-1} = n_j$ and $T_{j-1} = T_j$. Thus, Equations (5) and (6) may be combined to yield:

$$\frac{P_j \, (V_1+V_2)_j}{P_{j-1} \, (V_1)_{j-1}} = \frac{Z_j}{Z_{j-1}} \tag{7}$$

By defining $(V_1 + V_2)/V_1$ as the cell constant N_j, the following equation is obtained:

$$\frac{P_j}{P_{j-1}} = \frac{1}{N_j} \frac{Z_j}{Z_{j-1}} \tag{8}$$

Assuming that Z_j and Z_{j-1} approach unity when P_j approaches zero, then the Equation (5) reduces to

$$\lim_{P_j \to 0} \frac{P_j}{P_{j-1}} = \frac{1}{N_o} \tag{9}$$

or $\qquad N_o = \lim_{P_{j-1} \to 0} \frac{P_{j-1}}{P_j} \tag{10}$

where N_o is the cell constant at zero pressure only. For high pressure operation the effect on the cell constant caused by elastic deformation of the volumes must be included. For elastic deformation of a

thick-walled cylinder, the relative change in the volume of the

cylinder at any pressure is given by Lamé's formula in the following

equation:

$$\frac{\Delta V}{V} = \frac{P}{E} \left[2 \left\{ \frac{b^2 + a^2}{b^2 - a^2} + \mu \right\} + \frac{a^2 (1 - 2\mu)}{b^2 - a^2} \right] \tag{11}$$

where   a = Inner radius of the vessels

           b = Outer radius of the vessels

           μ = Poisson's ratio

           E = Modulus of elasticity

In terms of this relative change in volume, the true ratio

between pressures P_{j-1} and P_j is

$$N_j = \frac{(V_1 + V_2)_o}{(V_1)_o} \frac{(1 + \frac{\Delta V}{V}) P_j}{(1 + \frac{\Delta V}{V}) P_{j-1}} \tag{12}$$

or $N_j = N_o \dfrac{(1 + \alpha P_j)}{(1 + \alpha P_{j-1})}$ (13)

where $\alpha = \dfrac{1}{E} \left[2 \left\{ \dfrac{b^2 + a^2}{b^2 - a^2} + \mu \right\} + \dfrac{a^2 (1 - 2\mu)}{b^2 - a^2} \right]$ (14)

The value of α for the Burnett cell is estimated to be about

1.9×10^{-5} MPa^{-1}. When the best value of N_o has been determined the

value of N_j at any pressure P_j is obtained by Equation (13).

If the values of P_{j-1}/Z_{j-1} for j = 2,3,..... are successively

substituted into Equation (8) for the first expansion where j=1, the

following equation may be obtained:

$$\frac{P_o}{Z_o} = \lim_{P_j \to o} P_j N_j^j \tag{16}$$

Once the pressure data at the particular isotherm are measured, then it is possible to plot P_{j-1}/P_j versus P_{j-1} whose intercept will yield the cell constant, N_o, as indicated by Equation (10). Furthermore, knowing the value of N_o one can estimate N_j at any expansion by Equation (13). As a result, the run constant, P_o/Z_o, may be estimated by plotting $P_j N_j^j$ versus P_j as defined by Equation (16). Consequently, the gas compressibility factor may be estimated by the following equation:

$$Z_j = \left(\frac{P_o}{Z_o}\right)^{-1} P_j N_j^j \tag{17}$$

The compressibility factor of a gas may be expressed by a polynomial expansion using either the molar volume or the pressure as the independent variable:

$$Z = \frac{PV}{RT} = 1 + B\frac{1}{V} + C\frac{1}{V^2} + D\frac{1}{V^3} + \ldots \tag{18}$$

or

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \ldots \tag{19}$$

where B, C, D, ... and B', C', D', ... are called the second, third, fourth, ... virial coefficients and are dependent only on temperature for a pure gas. For historical reasons Equation (18) is known as the Leiden expansion and Equation (19) as the Berlin expansion. The relationship between the second virial coefficients in the Leiden and the Berlin expansions may be given in the following form:

$$B' = \frac{B}{RT} \tag{20}$$

Algebraic rearrangement of Equation (17) gives:

$$V (Z-1) = B + C \frac{1}{V} + D \frac{1}{V^2} + \ldots \tag{21}$$

At relatively low pressures, where V becomes large, terms involving the reciprocal of higher powers of V become progressively less important and in this region $V(Z-1)$ varies linearly with $1/V$.

If only the second virial coefficient is to be determined by using the expansions indicated in Equations (18) and (19), the Leiden expansion yields:

$$B = \lim_{1/V \to o} V(Z-1) \tag{22}$$

and the Berlin expansion yields:

$$Z = 1 + B' P \tag{23}$$

Thus it is possible to use experimental compressibility factors to evaluate the second virial coefficient for any particular isotherm by plotting $V(Z-1)$ versus $1/V$ or by plotting Z versus P whose intercept or slope yields B and B', respectively.

B. Experimental Study

B-1. Equipment

The Burnett equipment used for the compressibility measurements of carbonyl sulfide was essentially the same as that used by Robinson et al. (27) for their work on nitrogen-hydrogen sulfide mixtures. A schematic arrangement of the experimental apparatus is given in Figure 1.

Briefly, the Burnett cell consists of two constant volume vessels of different size fabricated from type 400 series stainless steel.
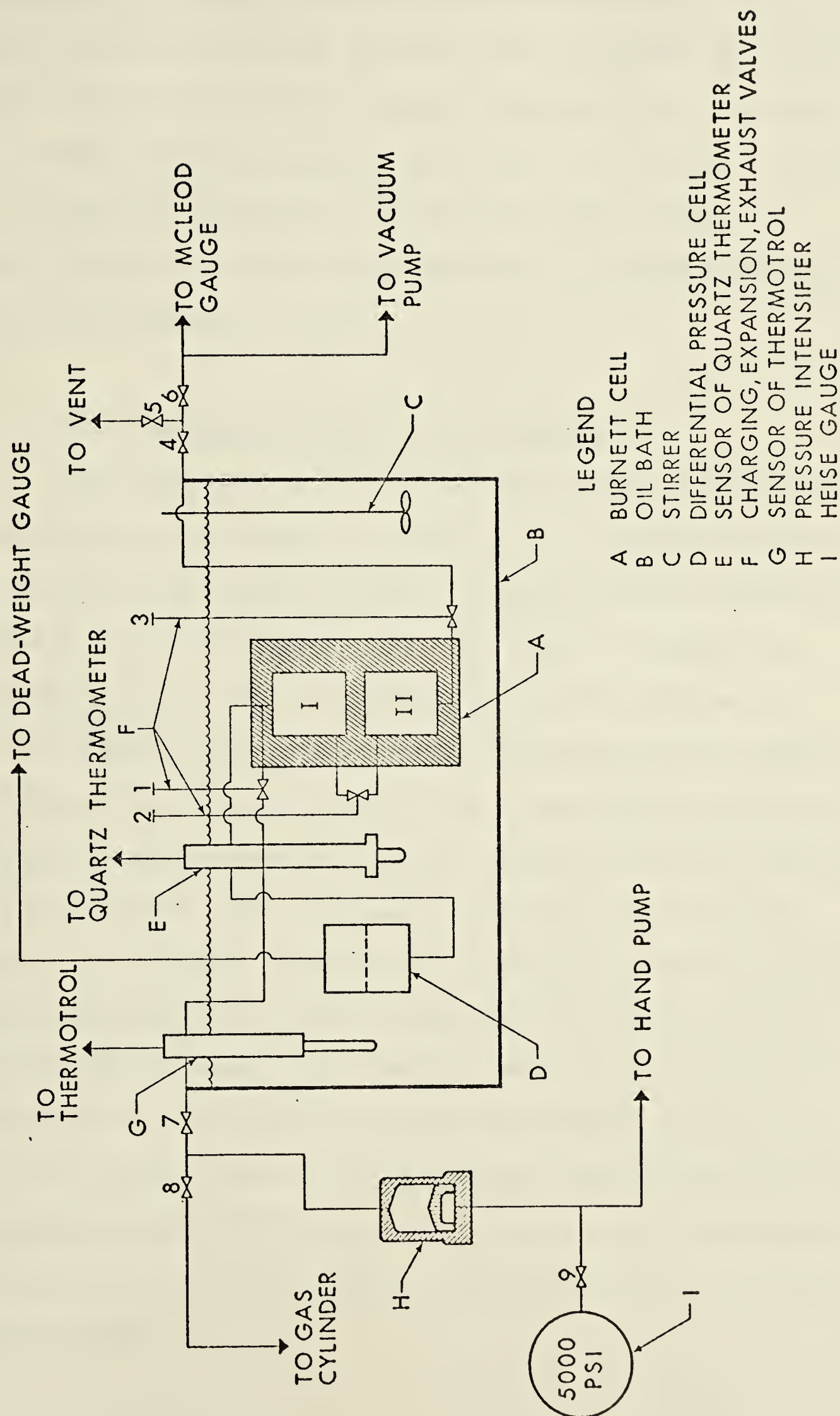
FIGURE 1. SCHEMATIC DIAGRAM OF EXPERIMENTAL BURNETT APPARATUS

LEGEND

A   BURNETT CELL
B   OIL BATH
C   STIRRER
D   DIFFERENTIAL PRESSURE CELL
E   SENSOR OF QUARTZ THERMOMETER
F   CHARGING, EXPANSION, EXHAUST VALVES
G   SENSOR OF THERMOTROL
H   PRESSURE INTENSIFIER
I   HEISE GAUGE

It is marketed as Model No. 2501-1 by the Ruska Instrument Corporation. The cell, along with its lead lines and valves, including the differential pressure cell was immersed in a constant temperature oil or ethanol bath depending on the temperature of the run. The bath was insulated with styrofoam and stirred by an electrically driven stirrer. A pressure intensifier coupled with a hand pump was used to charge the cell with the appropriate system.

B-2. <u>Temperature Control and Measurement</u>

The temperature of the bath was controlled by a Hallikainen Thermotrol temperature controller, Model No. 1053, capable of controlling the temperature within $\pm$ 0.005°C. A nickel resistance thermometer was used in the sensing element. The temperature of the bath was determined by using a Hewlett-Packard Company Quartz thermometer, Model No. HP-2801A, with a quartz crystal temperature sensor, Model No. HP-2850. The thermometer and its sensor have been calibrated at the factory by using techniques directly traceable to the U.S. National Bureau of Standards. Since the quartz thermometer sensor crystal exhibits a very linear, yet sensitive, correspondence between resonant frequency and temperature, only a conventional ice bath was used for calibration of the sensor. For the 323.2 and 383.2 K isotherms, the bath fluid consisted of Esso 10-W motor oil which was heated by two 1000 watt heaters. For the 273.2 K isotherm, the bath fluid consisted of denatured ethanol. This was cooled by copper coils through which denatured ethanol was also circulated from an auxiliary refrigerated temperature bath.

Using the thermotrol temperature controller and the quartz thermometer, the absolute accuracy of absolute temperature measurement is expected to be within $\pm$ 0.04 K.

B-3. Pressure Measurement

Pressure was measured with a Ruska Instrument Corporation dead-weight gauge. The dead-weight gauge was calibrated at the Ruska Instrument Corporation Laboratory with a master dead-weight gauge, which had been calibrated by the U.S. National Bureau of Standards. Pressure measurements were repeated several times to ensure that the constant pressure had been attained and that therefore equilibrium had been reached. Furthermore, time, room temperature, barometric pressure and temperature, and the load on the dead-weight gauge were recorded for each data point. The required calibration data for pressure corrections are listed in Part 1 of Appendix A.

The pertinent information on the instruments manufactured by the Ruska Instrument Corporation and used in the pressure measurements may be summarized in Table 1.

In this study, both the low and the high piston ranges of the dead-weight gauge were used. The overall estimated error in the measurement of pressure was $\pm$ 0.02 percent at pressures above 2428 pounds per square inch for the high pressure range piston cylinder assembly and increased to $\pm$ 0.05 percent for the low pressure range piston cylinder assembly.

TABLE 1

INFORMATION ON THE INSTRUMENTS USED FOR PRESSURE MEASUREMENTS FOR THE

VOLUMETRIC DATA OF CARBONYL SULFIDE

Instrument	Identification	Range
Ruska Dead-Weight Gauge	Cat. No. 2400-HL	Low: 6 to 2428 psi
	Ser. No. 12436	High: 30 to 12140 psi
Weights	Cat. No. 2402-HL	
	Ser. No. 12449	
Differential Pressure Cell	Cat. No. 2413	
	Ser. No. 12521	
Differential Pressure Null Indicator	Model No. 2416.2	
Manometer	Cat. No. 2409	
	Ser. No. 12608	
Hand Pump	Cat. No. 2461.1	
	Ser. No. 13546	

. B-4. Procedure

The experimental procedure used for obtaining the cell and

run constants, and for determining the compressibility factors of

carbonyl sulfide were the same. The procedure consisted of the following

steps:

1. Test the entire system for leaks.

2. Make the zero adjustment of the differential pressure cell 'D'.

3. Evacuate the system and flush it with the sample gas several times.

4. Charge the gas to the first vessel I of the Burnett cell at a required high pressure.

5. Attain steady temperature conditions for the entire system and measure the pressure while the second vessel is evacuating.

6. Expand the gas into the evacuated second vessel II and remeasure the pressure after thermal equilibrium is established.

7. Continue the expansions until a low pressure is reached so that extrapolations to zero pressure are possible.

Periods in the order of three hours or more were required to attain thermal equilibrium between expansions.

B-5. **Materials Used**

In this study, helium was used for calibrating the equipment and determining the cell constant. Helium was provided by the Consumers' Welding Supplies Ltd. of Canada with a nominal quoted purity of 99.995 mole percent. Carbonyl sulfide was used for determining the compressibility factors and was supplied on a special order by Matheson of Canada, Ltd. The results of Matheson's analysis of carbonyl sulfide is summarized as follows:

Component	Gas Phase Mole %	Liquid Phase Mole %
N_2	0.0052	0.0015
O_2	<0.0010	<0.0010
CH_4	0.0010	<0.0010
CO	0.0913	0.0082
CO_2	0.8800	0.2130
H_2S	0.4500	0.0340
CS_2	0.0051	0.0505
SO_2	<0.0010	<0.0010
COS	~98.6	~99.7

These results were rechecked and confirmed by a gas chromatographic analysis.

The liquid phase of the carbonyl sulfide cylinder was used for charging the system. It may be seen that the major impurity in the liquid phase was carbon dioxide.

C. Experimental Results and Discussion

C-1. Cell and Run Constants

Cell Constants, N_o

As mentioned previously, helium was used as the calibrating gas for the Burnett apparatus because it possesses linear isotherms up to moderately high pressures. Using the measured helium pressure data at each specified isotherm as presented in Appendix B, Table B-1, the zero pressure cell constants, N_o, for each isotherm are estimated by a linear least squares fit through P_{j-1}/P_j versus P_{j-1} points as plotted in Figure 2. The estimated N_o values for helium with 95% confidence limits are summarized in Table 2 below.
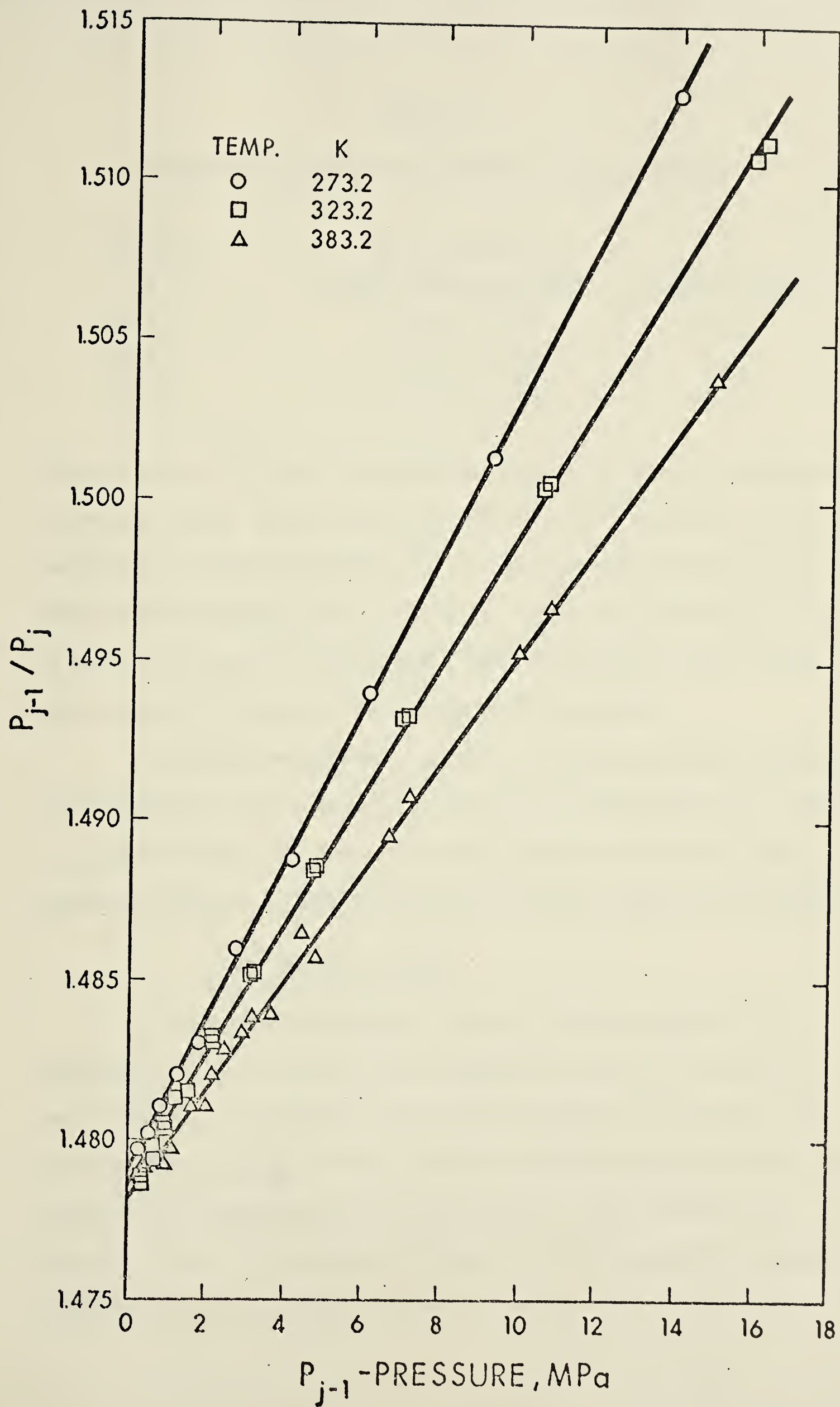
FIGURE 2. DETERMINATION OF BURNETT CELL CONSTANTS

TABLE 2

SUMMARY OF ESTIMATED CELL CONSTANT VALUES OF HELIUM

Isotherm K	Cell Constant, N_o $\pm$ 95% Confidence Limit	% Relative Error
273.2	1.4789 $\pm$ 0.0002	0.01
323.2	1.4785 $\pm$ 0.0002	0.01
383.2	1.4781 $\pm$ 0.0004	0.02

These values of the cell constant were used as a basis for determining corrected values of the cell constant at any j^{th} expansion for carbonyl sulfide by a similar procedure to that suggested by Canfield et al.(23) and given by Equation (13). N_o varied 3 parts in 1,000,000 at 273.2 K, 2 parts in 100,000 at 323.2 K and 1 part in 10,000 at 383.2 K when it was corrected by Equation (13) at each jth expansion.

Pressure measurements appear to be more sensitive and hence less accurate at low pressures as compared to high pressures. Therefore, it is most likely that the error in N_o estimates are due to these low pressure readings. These points can easily be recognized in Figure 2.

Run Constants, P_o/Z_o

Using the experimental carbonyl sulfide pressure data together with the corrected cell constants at each jth expansion for each particular isotherm as presented in Appendix B, Table B-2, the run constants, P_o/Z_o, at each isotherm are estimated by a linear least squares fit through the set of points of $(P_j, P_j N_j^j)$ as given in Figures 3 and 4. The estimated values of run constants for carbonyl sulfide with 95% confidence limits are presented in Table 3 below.
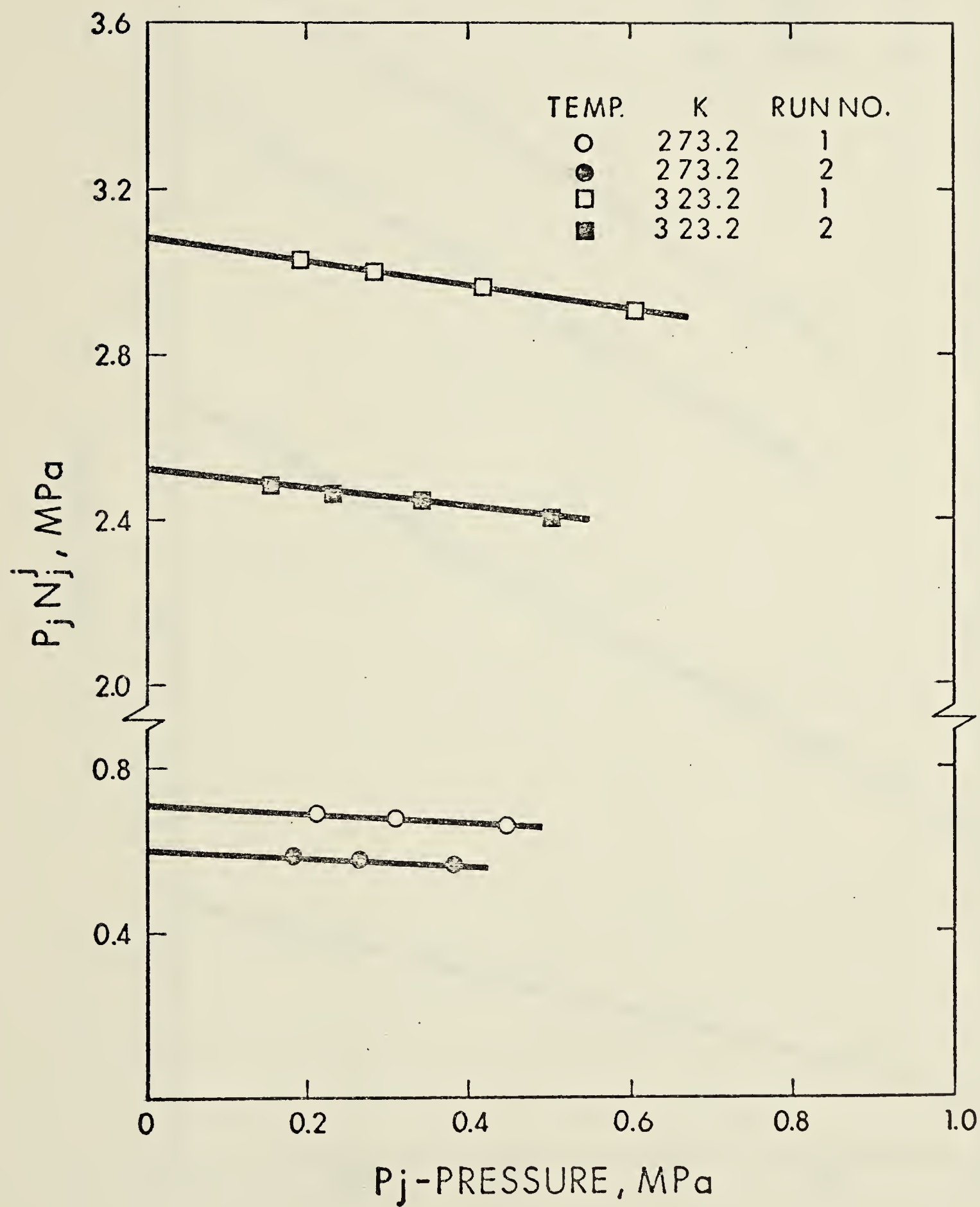
FIGURE 3. DETERMINATION OF BURNETT RUN CONSTANTS
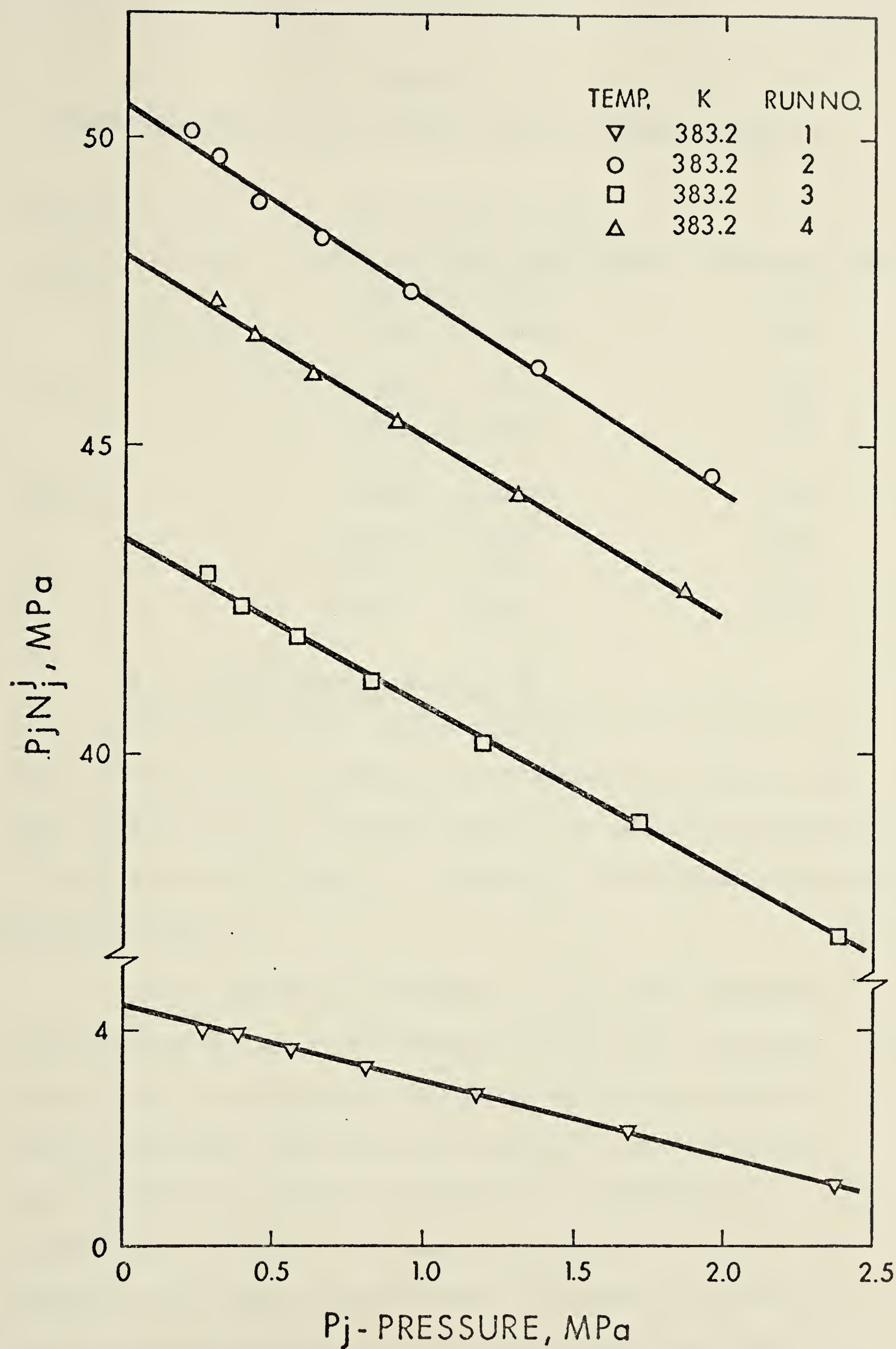
FIGURE 4. DETERMINATION OF BURNETT RUN CONSTANTS

TABLE 3

SUMMARY OF ESTIMATED RUN CONSTANT VALUES OF CARBONYL SULFIDE

Isotherm K	Run No.	Run Constant, P_O/Z_O ± 95% Confidence Limit (MPa)	% Relative Error
273.2	1	0.71369 ± 0.00788	1.10
	2	0.60116 ± 0.00618	1.03
323.2	1	3.0872 ± 0.0014	0.04
	2	2.5236 ± 0.0027	0.11
383.2	1	4.0845 ± 0.0075	0.18
	2	50.322 ± 0.070	0.14
	3	43.415 ± 0.074	0.17
	4	48.017 ± 0.154	0.32

C-2. Compressibility Factors, Z

Using the carbonyl sulfide experimental data presented in Table B-3 of Appendix B together with appropriate run constants, the compressibility factors of carbonyl sulfide are calculated by Equation (17) and tabulated in Table B-3 of Appendix B. These results are also plotted in Figure 5.

It was considered worthwhile to indicate the saturation curve on Figure 5. As a first attempt to do this, the two phase density data of Partington and Neville (2) which were reported at selected saturation temperatures were used with the corresponding experimental vapor pressure from Section IV to calculate the compressibility factors. When these values plotted on Figure 5 they exhibited a very large scatter and were, therefore, not useful for locating the saturation curve. As a second attempt, and in the absence of any more complete information the compressibility factor
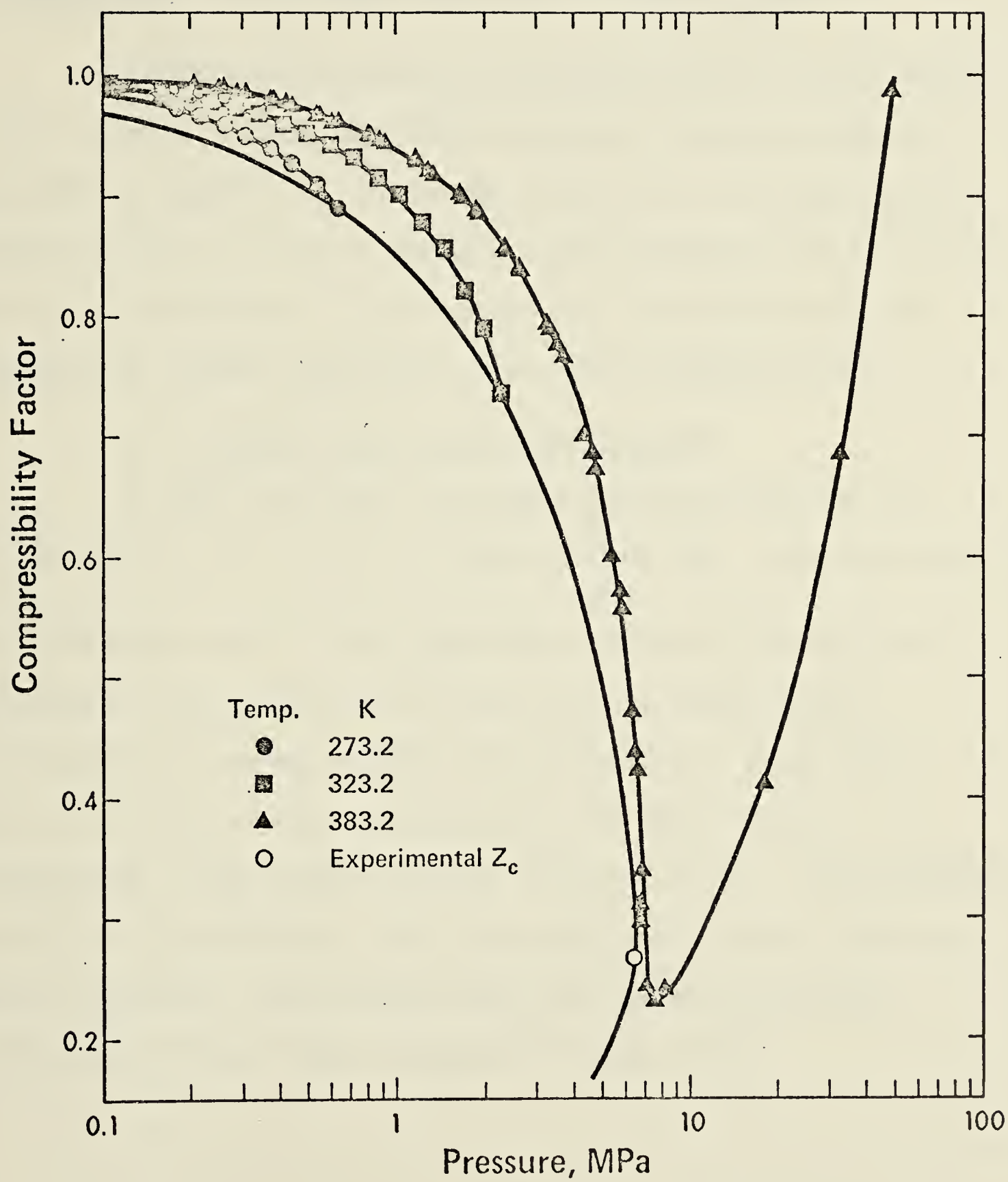
FIGURE 5. COMPRESSIBILITY FACTORS OF CARBONYL SULFIDE

curves at 273.2 and 323.2 K were extrapolated to the point of inter-section with the corresponding vapor pressures. These points together with the experimental critical point were then joined by a smooth curve to approximate the saturation conditions as shown in Figure 5.

The expected maximum error in compressibility factors at the lowest, highest, and the intermediate pressures for each isotherm are presented in Appendix C. The average percent error in compressibility factors at 273.2 K, 323.2 K, and 383.2 K are estimated to be 1.12, 0.16, and 0.47, respectively. It is expected that the actual errors are considerably somewhat less than these estimated maximum errors.

C-3. Second Virial Coefficients, B and B'

In order to estimate the second virial coefficients the Leiden, Equation (22), and the Berlin, Equation (23), expansions were used.

The appropriate data for this purpose are tabulated in Table B-3 of Appendix B. Using Equations (22) and (23), the second virial coefficients of carbonyl sulfide were estimated by a linear least squares fit of the data for $V(Z-1)$ versus $1/V$ and Z versus P, respectively. These plots are given in Figures 6 and 7. The estimated second virial coefficients B for the Leiden expansion and B' for the Berlin expansion at each isotherm with 95% confidence limits are summarized in Tables 4 and 5 which follow respectively.
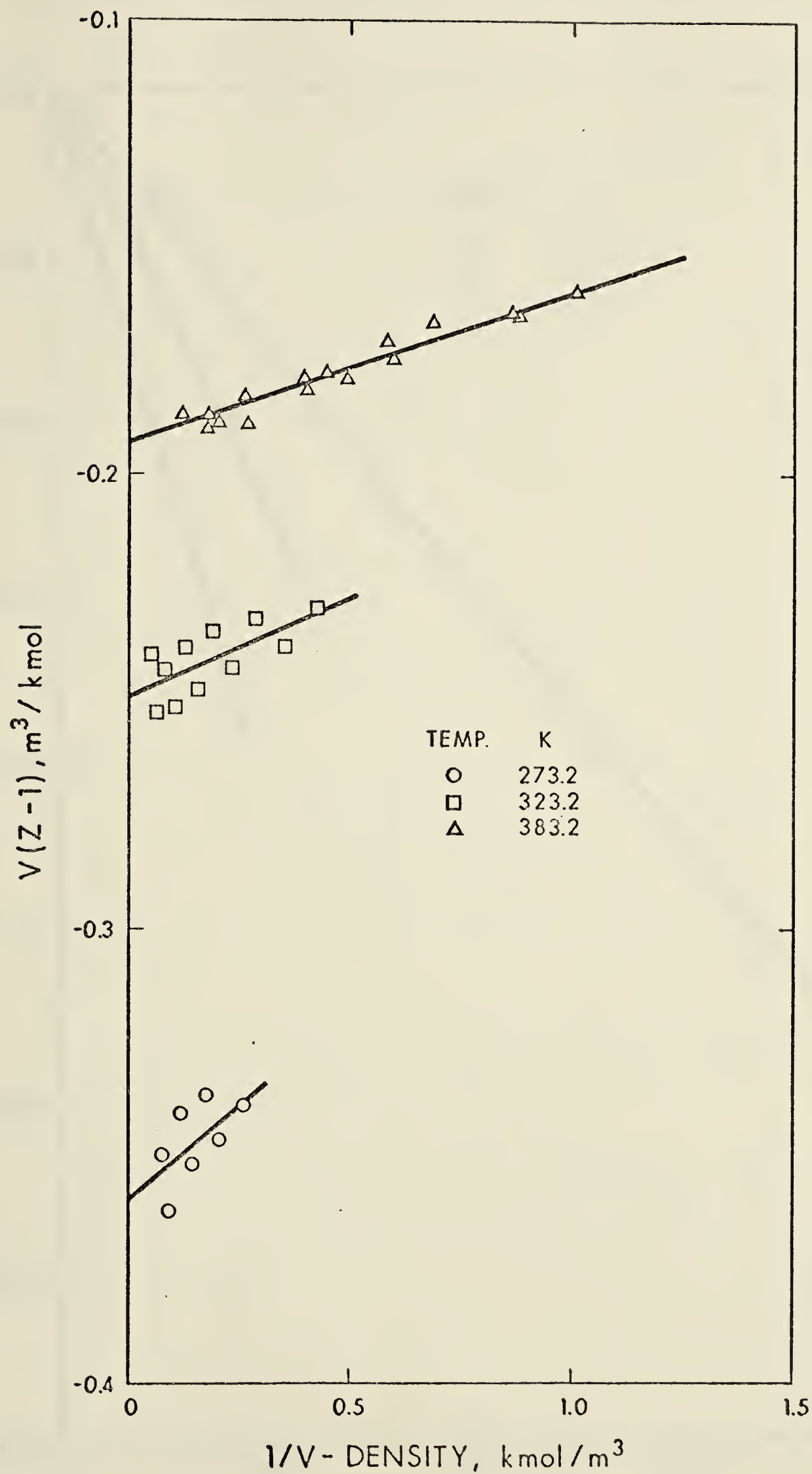
FIGURE 6. DETERMINATION OF THE SECOND VIRIAL COEFFICIENTS OF CARBONYL SULFIDE BY THE LEIDEN EXPANSION
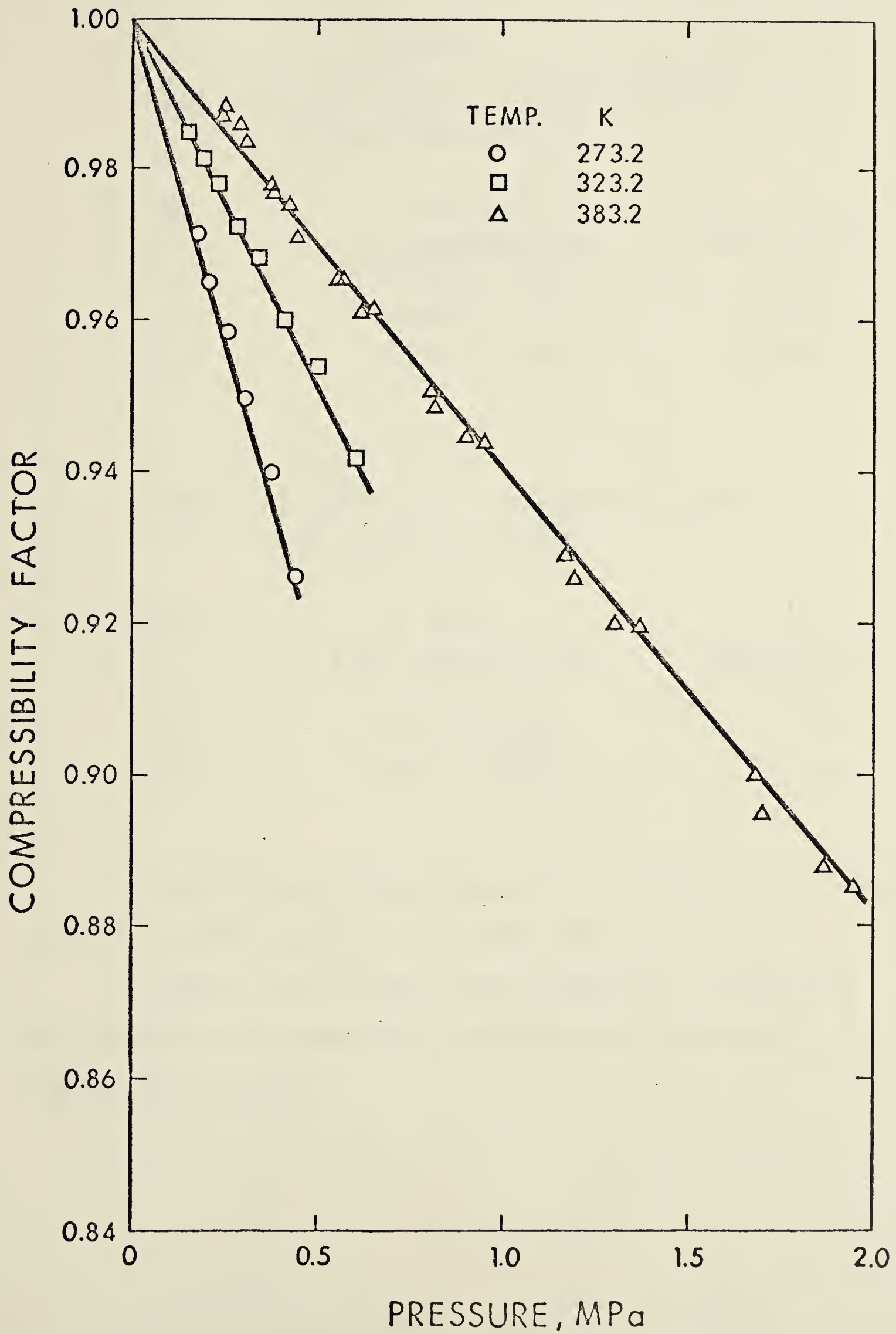
FIGURE 7. DETERMINATION OF THE SECOND VIRIAL COEFFICIENTS OF CARBONYL
SULFIDE BY THE BERLIN EXPANSION

TABLE 4

SECOND VIRIAL COEFFICIENT B FOR CARBONYL SULFIDE
BY THE LEIDEN EXPANSION

Isotherm K	B (m^3/ kmol) $\pm$ 95% Confidence Limit	% Relative Error
273.2	-0.3593 $\pm$ 0.0208	5.79
323.2	-0.2491 $\pm$ 0.0076	3.05
383.2	-0.1912 $\pm$ 0.0028	1.46

TABLE 5

SEOND VIRIAL COEFFICIENT B' FOR CARBONYL SULFIDE
BY THE BERLIN EXPANSION

Isotherm K	B' (MPa^{-1}) $\pm$ 95% Confidence Limit	% Relative Error
273.2	0.1641 $\pm$ 0.0154	9.36
323.2	0.09536 $\pm$ 0.00551	5.78
383.2	0.06131 $\pm$ 0.00151	2.46

The difference between two methods is estimated to be 3.76% at 273.2 K, 2.89% at 323.2 K, and 3.19% at 383.2 K.

The two sets of second virial coefficients, estimated by the Leiden and Berlin expansions, are plotted as a function of temperature in Figure 8.
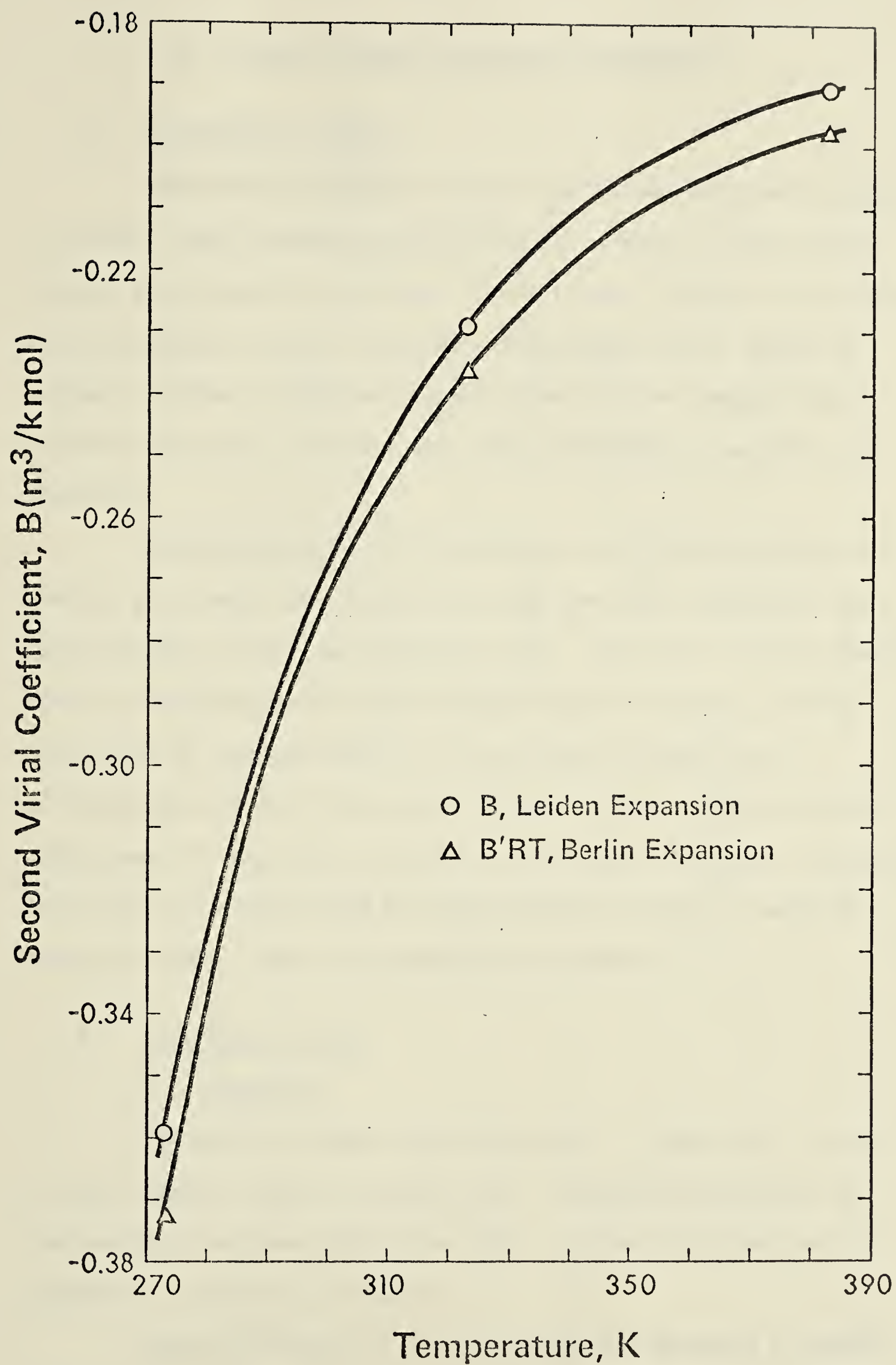
FIGURE 8. VARIATION OF SECOND VIRIAL COEFFICIENTS WITH
TEMPERATURE FOR CARBONYL SULFIDE

IV - VAPOR PRESSURE AND CRITICAL PROPERTIES

A.   Experimental Method

The vapor pressure of carbonyl sulfide was obtained by using a constant volume windowed equilibrium cell similar to that used in typical high pressure liquid level installations. Briefly, the method involved making a series of pressure measurements for a sample of carbonyl sulfide at different predetermined constant temperatures provided there was a visible vapor-liquid interface, a meniscus, in the cell.

Different methods for determining the critical properties of several gases were summarized by Kobe and Lynn (12), Rowlinson (30), and Kudchadker, Alani, and Zwolinski (31). Consistent with the method used for establishing the vapor pressure curve of carbonyl sulfide, the method of "disappearance of the meniscus" has been used to establish the critical values for carbonyl sulfide. It involved the measurement of temperature, pressure, and volume of carbonyl sulfide at the critical condition when the vapor-liquid interface or meniscus became invisible; that is the meniscus disappeared.

B.   Experimental Study

B-1. Equipment

The constant volume equilibrium cell is essentially the same as that recently used by Wu et al. (28). A detailed description of the equipment has been given by Wu (29). A schematic layout of the equipment is presented in Figure 9.

The equilibrium cell A was based on the design of a typical high pressure liquid level gauge. The body was made from type 316
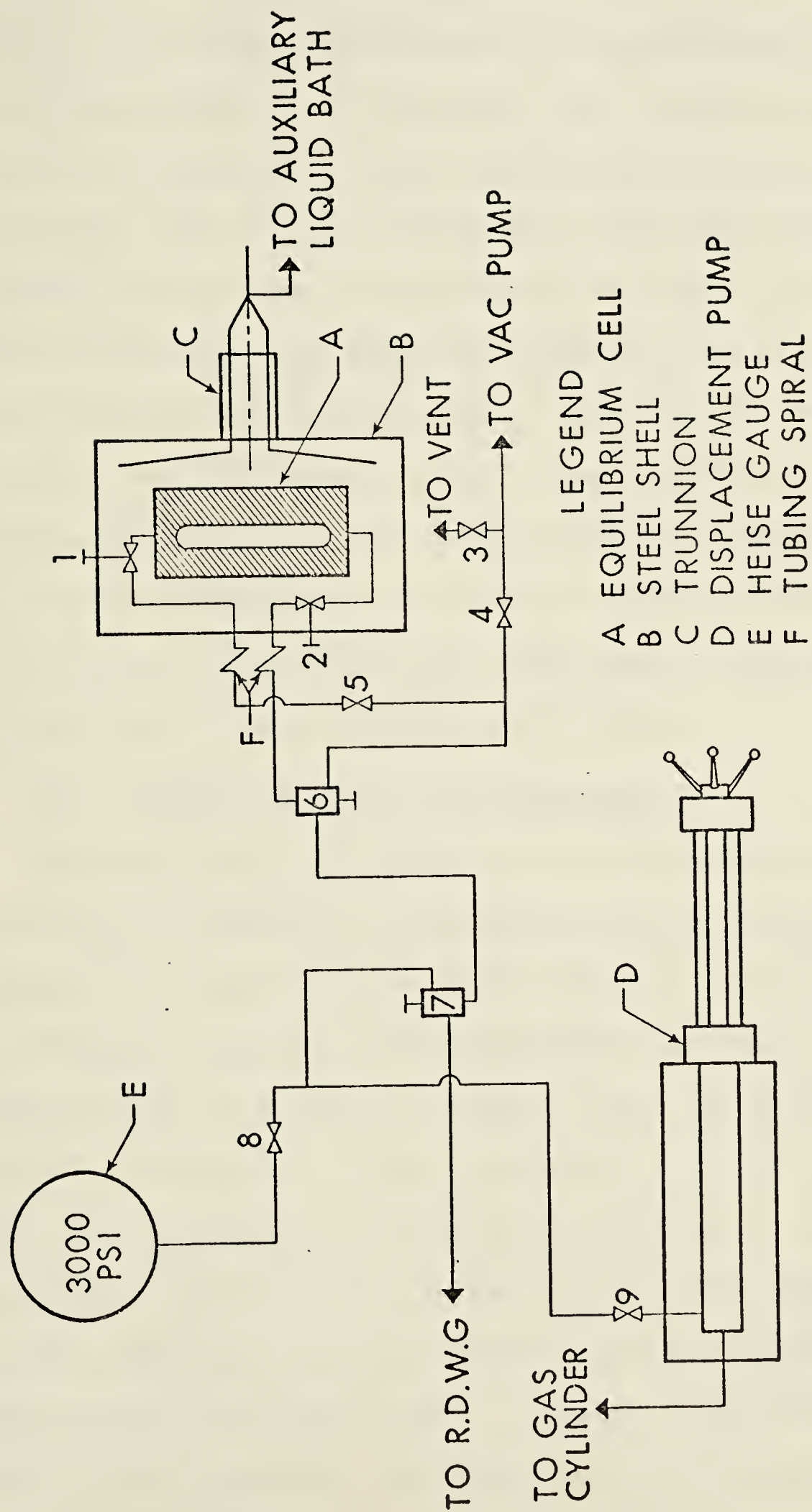
FIGURE 9. SCHEMATIC DIAGRAM OF EQUIPMENT USED FOR MEASURING THE VAPOR PRESSURE AND CRITICAL

PROPERTIES OF CARBONYL SULFIDE

LEGEND

A EQUILIBRIUM CELL
B STEEL SHELL
C TRUNNION
D DISPLACEMENT PUMP
E HEISE GAUGE
F TUBING SPIRAL

TO AUXILIARY
LIQUID BATH

TO VAC. PUMP

TO VENT

TO R.D.W.G.

TO GAS
CYLINDER

3000
PSI

stainless steel. The design working pressure for the cell was 15 500 kPa at 310 K. Two tempered borosilicate glass windows were mounted on both the front and back faces of the cell. The cell was enclosed in a steel shell B which has two glass windows placed on both the front and back faces. Both the cell and the steel shell were mounted on the trunnion C to the right of the main cell as shown in Figure 9. The trunnion was connected to an agitation mechanism driven by a motor where the eccentric shaft could be used to rotate the cell and its contents back and forth through an angle of approximately 30 degrees. The cell was connected to the gas cylinder through a displacement pump having a volume of about 100 ml and capable of reading volumes nearest to 0.01 ml. The cell was also connected to a dead-weight gauge and a vacuum pump through appropriate steel tubing.

B-2. Temperature Control and Measurement

The equilibrium cell temperature was maintained at the required value by circulating a fluid from an auxiliary controlled temperature bath through the space between the cell and the steel shell. Triethylene glycol and denatured ethanol were used as circulating fluids for temperature ranges of about 298 to 378 K and 265 to 298 K respectively. The bath was heated by two 1000 watt heaters. Bath temperatures up to 333 K were controlled by a bimetallic strip controller manufactured by the American Instrument Company, model 4-235. This could be set to control either the refrigerator or the heater but not both simultaneously. However, a Hallikainen Instrument Company thermotrol, model 1053, was used to control the temperatures above 333 K.

Once a constant temperature was attained, a copper-Constantan thermocouple, connected to a digital voltmeter, was used to measure its value. The thermocouple was calibrated against a Leeds and Northrup platinum resistance thermometer, model 8163, which has been calibrated by the National Research Council of Canada. The calibration of the thermocouple is shown below:

Temp. (K)	TC Error, ΔT
273.15	+ .178
293.616	+ .108
327.699	- .028
352.395	- .314
375.829	- .491

where ΔT is the temperature difference between the resistance thermometer reading and the thermocouple reading. The cell temperature could be controlled to within $\pm$ 0.1°C using these instruments.

B-3. Pressure Measurement

Pressures were measured by a Ruska Instrument Corporation dead-weight gauge. The dead-weight gauge calibration and data recording were the same as that of described in Section III. The liquid level of carbonyl sulfide in the cell was also recorded at each data point of the particular isotherm. The required pressure correction data are listed in Part 2 of Appendix B.

The pertinent information on the instruments manufactured by the Ruska Instrument Corporation and used in the pressure measurements may be summarized in Table 6.

TABLE 6

INFORMATION ON THE INSTRUMENTS USED FOR PRESSURE MEASUREMENTS FOR THE

VAPOR PRESSURE OF CARBONYL SULFIDE

Instrument	Identification	Range
Ruska Dead Weight Gauge	Cat. No. 2400HL Ser. No. 8338	Low: 6 - 2448 psi High: 30 - 12140 psi
Weights	Cat. No. 2400HL Ser. No. 8338	
Differential Pressure Cell	Cat. No. 2437-705 Ser. No. 16268	
Differential Pressure Null Indicator	Model 2416.2	
Manometer	Cat. No. 2409 Ser. No. 8256	
Hand Pump	Cat. No. 2400 HL Ser. No. 8338	

In this work, the low range piston of the Ruska dead-weight gauge was used and pressures were measured to within $\pm$ 0.05%.

B-4. Volume Measurement

It was necessary to measure the volumes of both the equilibrium cell and the tubing between the cell connection (valve No. 2) and the dead-weight gauge. The experimental observations and calculated volumes are reported in detail in Appendix D.

The volume of the equilibrium cell was measured by using weighed amounts of mercury at room temperature and it was found to be 74.704 ml. The volume of the tubing was measured as follows: First, pure nitrogen was placed in the tubing at known room temperature and some appropriate pressure while valve No. 2 was closed and the

equilibrium cell was evacuated. Secondly, valve No. 2 was opened and nitrogen was expanded into the new system which included the tubing plus the cell volume. After a short period of time, a new system pressure and temperature were reached and they were also recorded. By using the thermodynamic property data on nitrogen together with the already known equilibrium cell volume, the tubing volume was calculated and found to be 10.609 ml.

Knowing the volumes of the equilibrium cell and tubing, it was possible to find the amount of carbonyl sulfide in the system at any given pressure and temperature.

B-5. Procedure

Firstly, the equipment was evacuated and flushed with carbonyl sulfide several times. About 30 ml of liquid carbonyl sulfide from the supply cylinder was then added to the displacement pump. During this operation, a bath around the pump was filled with ice and valve No. 9 was closed. Following the addition of carbonyl sulfide, the supply cylinder valve was shut off.

Secondly, carbonyl sulfide was introduced into cell A by opening valves No. 9, 7, 6, and 2. Later on, valve 9 was closed provided two phases were visible in the cell. Once the cell temperature was set and maintained at the required predetermined value, the vapor pressure of carbonyl sulfide was measured by using the dead-weight gauge. These measurements were repeated several times to ensure that the equilibrium conditions were attained in the cell.

Thirdly, the vapor-liquid interface was observed very closely. As long as an interface was visible in the cell, a new set of vapor

pressure measurements were carried out at another temperature. This was continued until the critical condition was approached.

At this point the vapor-liquid interface became unstable and upon agitation the cell contents became frothy and turbulent. The bubbles and droplets cleared slowly and ultimately disappeared with the formation of a flat meniscus that could best be observed by reflected light.

Since the original charge of COS in the cell exceeded the mass corresponding to the critical volume, the meniscus tended to form near the top of the cell. The required amount was finally obtained by a trial and error procedure which involved the controlled removal of small amounts of the liquid phase until the meniscus appeared exactly at the middle of the cell.

The sequence of removing COS from the cell, and increasing the temperature incrementally was continued until agitation of the cell contents resulted in the formation of a completely opaque dispersion. After a considerable period of time lasting as much as an hour or so, this dispersion cleared slowly from both the top and the bottom until all of the bubbles and/or droplets disappeared at the middle of the cell in the absence of any observable meniscus. This condition was taken as the critical temperature and pressure. The condition was reproducible within about $\pm$ 0.02 K and $\pm$ 2 kPa.

The phenomenon of critical opalescence and the characteristic bright red color in transmitted light prevailed throughout the period of observation in the vicinity of the critical point.

In order to determine the critical volume, the following procedure was followed. Valve No. 2 at the base of the cell was

closed and the contents of the connecting lines up to valve No. 7 were purged. A stainless steel bomb having a capacity of about 45 ml was then connected to valve No. 7 and the bomb and tubing system was thoroughly evacuated while keeping the bomb in an ice bath. The temperature of the cell contents was then held at 323.2 K with the resulting formation of two phases at the vapor pressure. When this condition had been reached, valve No. 2 was opened and the contents of the equilibrium cell were allowed to expand into the bomb and tubing system where the carbonyl sulfide condensed in the bomb at 273.2 K under the corresponding vapor pressure. The amount of carbonyl sulfide collected in the bomb was determined by weighing. The amount of carbonyl sulfide remaining in the equilibrium cell and the connecting lines up to valve No. 7 was calculated from the known volume, pressure, and temperature using the molal density previously determined at 323.2 K in the Burnett experiments.

The measurements and calculations related to the determination of the critical volume are reported in Appendix D.

B-6. Materials Used

The carbonyl sulfide used to determine the critical properties and to establish the vapor pressure curve was provided by the Synthatron Corporation of U.S.A. The material had the following liquid phase composition:

Content	Mole %
Carbonyl Sulfide	99.952
Carbon Dioxide	0.027
Air	0.021

C. Experimental Results and Discussion

C-1. Vapor Pressure of Carbonyl Sulfide

The vapor pressure of carbonyl sulfide was determined at temperatures ranging from 264.5 K to the critical point. The results are summarized in Table E-1 of Appendix E.

The vapor pressure curve of carbonyl sulfide is presented in Figure 10. The experimental vapor pressure data of carbonyl sulfide were fitted to yield the following approximation for the range 264.5 - 378.9 K:

$$\log_{10} P = \frac{-1226.941}{T} + 8.976264 - 8.744328 \times 10^{-3} T$$
$$+ 9.592933 \times 10^{-6} T^2 \tag{24}$$

where P is in kPa. The average absolute error of the fit is calculated to be 0.07 percent. This shows that there is a good agreement between experimental data and the fitted approximation presented as Equation (24).

Earlier work of Kemp and Giauque (1) gave the experimental vapor pressure data of carbonyl sulfide for the low temperature range 161.8 - 233.8 K. Equation (2) represents the fitted approximation obtained by using these data. The average percent error in their fit is calculated to be 0.03.

It may be interesting to note that Equation (24) reproduces the Kemp and Giauque's data with an average error of 1.15 percent. Moreover, the following equation was obtained by fitting the total experimental data of Kemp and Giauque and this work for the whole temperature range 161.8 - 378.8 K:
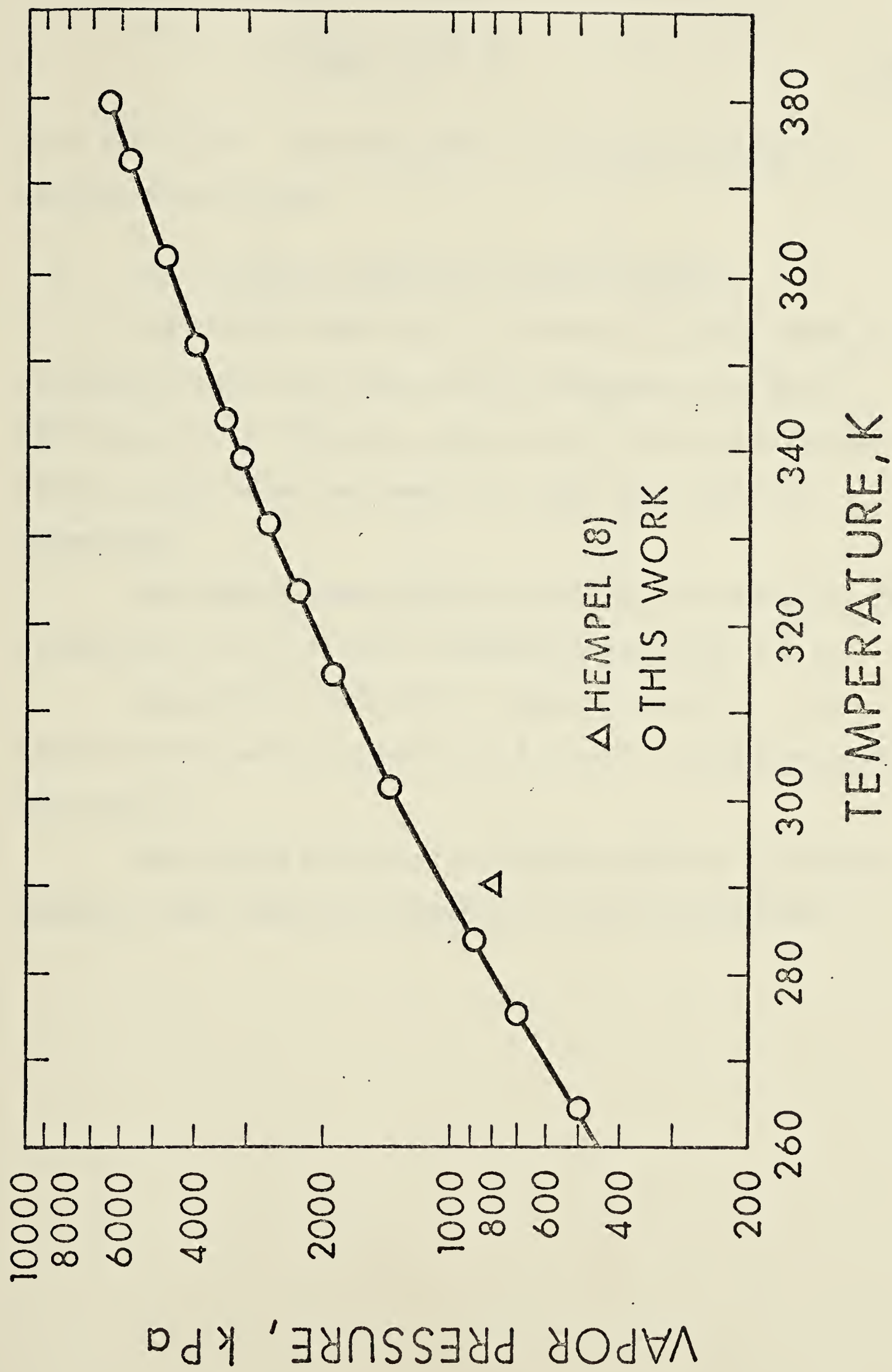
FIGURE 10. VAPOR PRESSURE OF CARBONYL SULFIDE

$$\log_{10} P = \frac{-1255.761}{T} + 9.346479 - 1.019333 \times 10^{-2} T$$

$$+ 1.137583 \times 10^{-5} T^2 \tag{25}$$

where P is in kPa. The average error of this approximation is calculated to be 0.19%.

C-2. Critical Properties of Carbonyl Sulfide

The critical temperature, T_c, pressure, P_c, and volume, V_c, of carbonyl sulfide were experimentally determined to be 378.8 K, 6349 kPa, and 0.135 m^3/kg mol, respectively. The expected maximum errors in these values are found to be 0.04%, 0.1%, and 0.4%, respectively.

The critical compressibility factor, Z_c, of carbonyl sulfide is calculated to be 0.272 with a maximum expected error of 0.5%.

Using Pitzer's definition the acentric factor, ω, of carbonyl sulfide was calculated to be 0.096 with a maximum expected error of 0.1%.

The measured and estimated critical properties of carbonyl sulfide by other workers are summarized in the following Table 7.

TABLE 7

SUMMARY OF CRITICAL PROPERTIES OF CARBONYL SULFIDE

Author(s)	T_c (K)	P_c (kPa)	V_c (m³/kmol)
Hempel (8) (measured)	378.2	6384	
Ilosvay (9) (measured)	378.2		
Partington and Neville (2) (measured)	375.4		
Kobe and Lynn (12) (estimated)		6181	0.138
Lydersen (13) (estimated)	378	6586	0.134
Zandler et al.(21) (estimated)	409.1	8319	0.149
Miranda (5) (estimated)	386.2	6619	
This Work (measured)	378.8	6349	0.135

V - REFRACTIVE INDEX MEASUREMENTS

A. Experimental Method

The method used for experimentally measuring the refractive index of carbonyl sulfide was based on the following facts. If a transparent glass window with parallel faces and a mirror are located at a known angle to each other, a ray of light striking the outer glass surface at right angles will be reflected from the surface along the line of travel. In addition, the ray of light will also go through the glass be refracted, strike the mirror be reflected, and then emerge from the original glass surface at an angle which may be directly related to the refractive index of the material between the window and the mirror. In this work, the window and mirror formed part of a high pressure vapor-liquid equilibrium cell and the necessary ray of light was a Helium-Neon gas at a wavelength of 6328 Å.

A-1. Refraction

When light travels from one medium to another, it undergoes a change of velocity, and if the angle of incidence is not 90°, there will be a change in direction. This phenomenon is commonly known as refraction.

Figure 11 is a schematic representation of the angle measurements involved in the determination of the refractiv index. The angle γ is measured by autocollimation and from Snell's law of refraction it follows that:

$$n_1 \sin \gamma = n_2 \sin \beta \qquad (26)$$

$$n_2 \sin \beta = n_3 \sin \delta \qquad (27)$$

$$\therefore n_3 = n_1 \sin \gamma / \sin \beta \qquad (28)$$
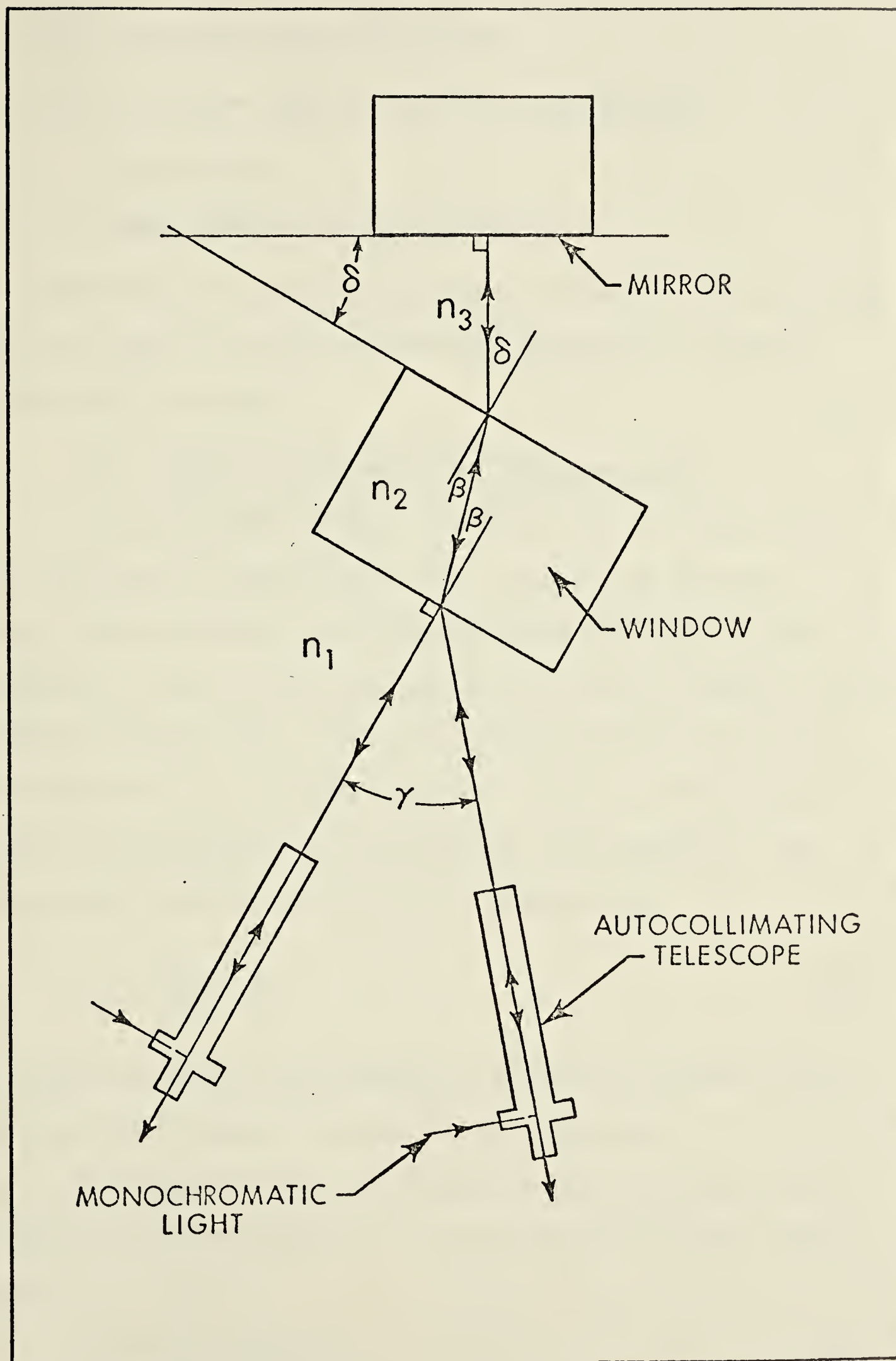
FIG. 11. SCHEMATIC REPRESENTATION OF THE ANGLE MEASUREMENT
INVOLVED IN THE DETERMINATION OF THE REFRACTIVE INDEX

where

n_1 = refractive index of the ambient air

n_2 = refractive index of the glass

n_3 = refractive index of the fluid being measured

δ = prism angle

γ = angle measured by autocollimation

For a light source of given wavelength, n_1 is known, δ can be measured if $n_3 = n_1$, that is, if the cell contains ambient air, and hence, n_3 can easily be measured.

A-2. Density Measurement from Refractive Index

The relationship between refractive index and density was first introduced by Newton (32) in 1704. Since then, numerous formulae relating density and refractive index have been proposed. A comprehensive review of the more relevant refractivity formulae has been reported by Besserer (33). One of the proposed formulae by Lorentz (34) and Lorenz (35) is widely accepted in optical physics mainly because it can be related to the electronic polarizability. The Lorentz-Lorenz formulation was given by Equation (4).

$$R_{LL} = \frac{n^2-1}{n^2+2} \; \frac{1}{\rho} \tag{4}$$

For a given substance, this function is essentially constant, showing only very slight changes with pressure and temperature.

Buckingham and Pople (36) proposed that the Lorentz-Lorenz refractivity could be written in a virial expansion in molar volume, namely

$$R_{LL} = R_{LL}^{\circ} + \frac{B}{V} + \frac{C}{V^2} + \; . \; . \; . \; . \; . \tag{29}$$

where R_{LL}° is the molar refractivity at zero density and B and C are the second and third virial refractivity coefficients respectively. In order to find R_{LL} by using Equation (29), one should have very accurate density data, because B and C are very sensitive to accuracy of density data. If there is not enough accurate volumetric data then R_{LL} can be calculated as a linear function of pressure because during the experimental study only pressure and refractive index are measured. R_{LL} could be written in the following form:

$$R_{LL} = R_{LL}^{\circ} + mP \tag{30}$$

where R_{LL}° is the molar refractivity at zero pressure and m is the molar refractivity pressure coefficient.

Once the refractive index measurements have been obtained it becomes possible to calculate the molar refractivity using the known density data. The molar refractivity values obtained along each isotherm can then be fitted as a linear function of pressure, Equation (30), and R_{LL}° determined at zero pressure.

Alternatively, Equation (4) can be written as:

$$\rho = \frac{n^2-1}{n^2+2} \frac{1}{(R_{LL}^{\circ}+mP)} \tag{31}$$

Therefore, the densities of a substance at each isotherm can be estimated by using the Lorentz-Lorenz formulation with the calculated molar refractivities and the measured refractive indices.

B.   Experimental Study

B-1. Equipment

A detailed description of the equipment design has been presented previously by Besserer (33). Although no significant

modification has been made to the original design, it is considered desirable to mention some of the more pertinent features here. Much of the description of the equipment and the optical system has been taken from a paper by Besserer and Robinson (37).

A schematic diagram of the apparatus and its associated equipment is shown in Figure 12 and the essential features of the cell design are shown in Figure 13. The equilibrium cell has an overall length of 0.48 m and was machined from a 0.10 m diameter type 316 stainless steel cylinder. The cell proper consists of three parts, two cylinder-piston sections and a central windowed section. The three sections are bolted together with the high pressure seals between them made by flattened teflon-O-rings. Each piston has a 0.10 m travel and is confined to its respective cylinder. The function of the pistons is to isolate the cell contents from the hydraulic fluid, a low viscosity silicone oil, and to provide a means for varying the cell volume. The piston seal is effected by four neoprene-O-rings. The two pistons are hydraulically driven by a motorized dual cylinder high pressure pump with an opposed transmission (Ruska model 2248 WII).

A horizontal section A-A through the center of the cell shows how the window, a pyrex glass disk 0.029 m in diameter and 0.025 m thick with its face flat and parallel to $\pm 10^{-2}$ m, and a type 316 stainless steel mirror form the boundaries of a 30° prism. The window and mirror are held in place by bolted cover plates and sealed against lapped surfaces with 1.5×10^{-3} m thick glass-filled teflon gaskets.

A second horizontal section B-B shows one of the sampling
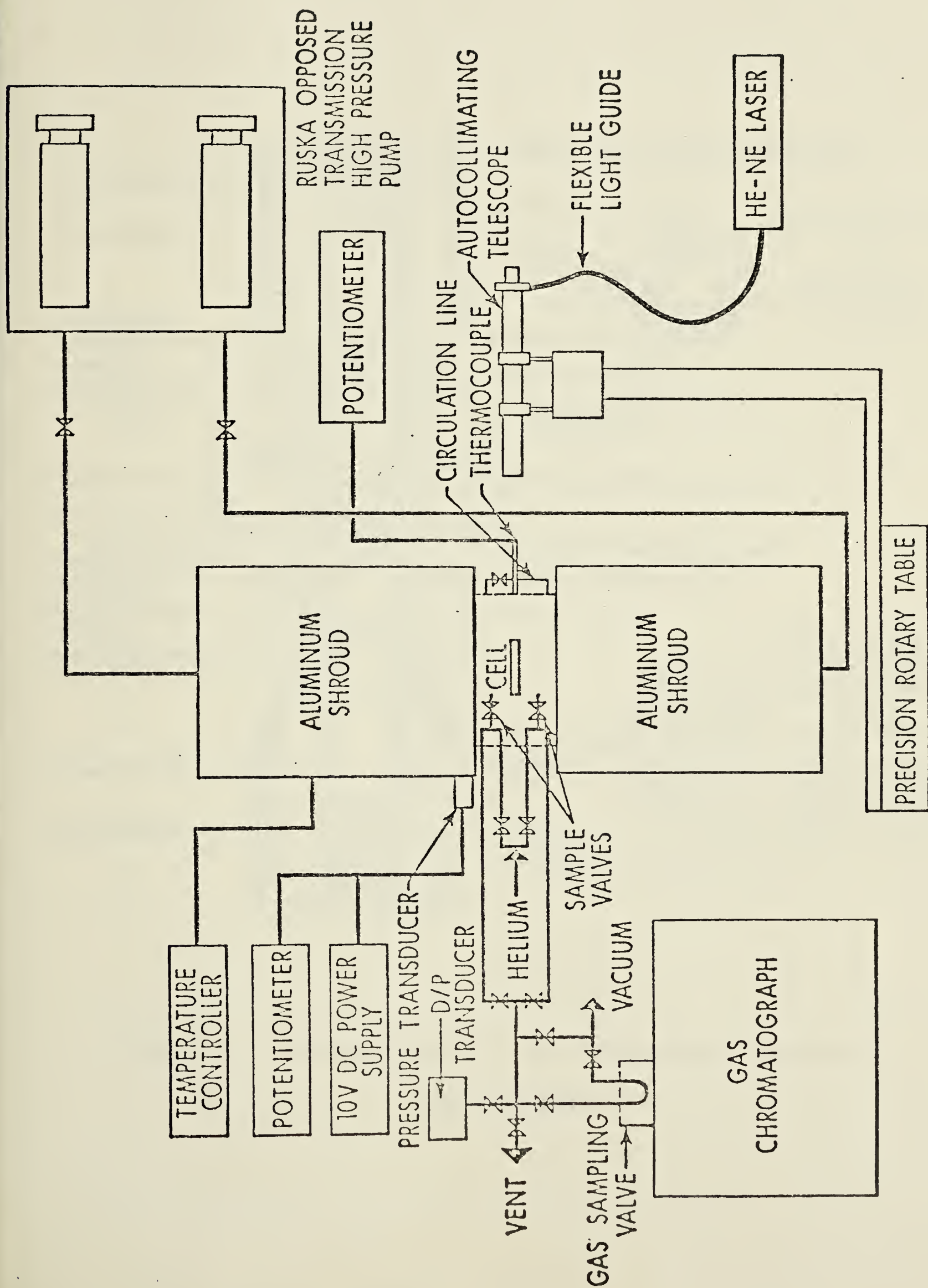
FIGURE 12. SCHEMATIC DIAGRAM OF THE CELL AND ITS ASSOCIATED EQUIPMENT USED FOR REFRACTIVE INDEX MEASUREMENTS

COOLING COIL

STRIP HEATER

ALUMINUM
ENVIRONMENTAL
SHROUD

MOUNTING BOLT
SLOT

SAMPLE VALVE

THERMOCOUPLE

SAMPLE VALVE

ALUMINUM
ENVIRONMENTAL
SHROUD

MOUNTING BOLT
SLOT

STRIP HEATER

COOLING COIL

HYDRAULIC FLUID CONDITIONING COIL

SAMPLE LINE

SAMPLE
VALVE

SAMPLE LINE

CIRCULATION LINE
INLET

PRESSURE
TRANSDUCER

UPPER
PISTON

UPPER CYLINDER

PRESSURE
TRANSDUCER

SECTION B–B

CENTRAL WINDOWED SECTION

EXTERNAL CIRCULATION LINE

INTERNAL CHECK VALVE

LOWER CYLINDER

LOWER
PISTON

THERMO-
COUPLE

HYDRAULIC
FLUID
CONDITIONING
COIL

LINE 0.7 cm OFF
CYLINDER AXIS

WINDOW COVER
PLATE

PYREX WINDOW

STEEL DISK WITH
POLISHED SURFACE

DISK COVER PLATE

CENTRAL TO AXIS

SECTION A–A

FIGURE 13. ESSENTIAL FEATURES OF THE CELL USED FOR REFRACTIVE

INDEX MEASUREMENTS

valves, the pressure transducer port, and the circulation line outlet. The sampling valves are internally mounted Circle Seal MV-92 micrometering valves with provision made for flushing out and evacuation of the low pressure sampling line. The circulation system used to attain equilibrium consists of an internal check valve in the central section and an external 3.3×10^{-3} m diameter stainless steel line with shut-off valve.

B-2. Temperature Control and Measurement

The temperature of the equilibrium cell is maintained by two 0.15 m diameter aluminum environmental control shrouds which are placed over the ends of the cell as shown in Figure 13. Each shroud has four 150 watt strip heaters and a 6 m cooling coil. A Thermac proportional plus integral controller operates the heaters in both shrouds and controls the cell temperature to within $\pm$ 0.05 K of the set point.

When working at isotherms below ambient temperature (273.2 and 283.2 K), the cell was cooled by circulating ethylene glycol-water mixture refrigerated by Freon-12 and air refrigerated by denatured ethanol, respectively. At isotherms above ambient temperature (323.2, 343.2, 363.2, and 383.2 K) instrument air was used as a cooling fluid in the cooling coil.

The hydraulic fluid is preconditioned before it enters the cell by 2.5 m of high pressure tubing which has been coiled into each shroud.

The temperature was measured with an iron-Constantan thermo-couple sheathed in 316 stainless steel with its tip exposed to the fluid in the prism. The temperature is believed known to $\pm$ 0.1 K.

B-3. Pressure Measurement

The pressure was measured by a 3000 psi 316 stainless steel bourdon tube Heise gauge which had been calibrated by a Ruska dead-weight tester. The pressure is believed known to $\pm$ 3 psia.

B-4. Optical System

A telescope (Gaertner M523 aperture 0.28 m, f.l. 2.50 m) with an Abbe-Lamont autocollimating eyepiece (Gaertner 1372) was mounted on a 0.25 m diameter precision rotary table (Karl Kneise RTHP-10) with a two second vernier hand wheel and a maximum table error of 10 seconds in 360° of rotation. The table was centered under a point on the front surface of the pyrex cell window. Monochromatic light at a wavelength of 6328 $\overset{\circ}{A}$ is provided by a Helium - Neon gas laser (Spectra Physics model 132) and was transmitted to the eyepiece by a glass fiber light guide.

The refraction angle γ shown in Figure 11 was measured by autocollimation. The measured angles have a repeatability of $\pm$ 4 seconds and a table error of $\pm$ 2 seconds over the measured range. The refractometer has an overall possible error of $\pm$ 6 x 10^{-5} in the refractive index and a possible range of 1.0 to 1.7.

B-5. Procedure

The cell was evacuated and flushed with carbonyl sulfide several times. Approximately 50 ml of liquid carbonyl sulfide was introduced into the cell and then the bottom piston was drawn up as far as possible. (The possible working volume ranges from 10 to 174 ml.)

The required isotherm was attained. In order to be sure that equilibrium had been achieved, the line image in the liquid phase through the autocollimating telescope and the temperature were

observed very closely. The image was very sensitive to temperature
fluctuations and would not become stable until the equilibrium state
had been attained. The angle γ was measured by observing the location
of the line image obtained through normal light incidence on the glass
window and the mirror at pressures ranging from the possible lowest
pressure of the liquid phase to about 20 684 kPa. The pressure was
increased to the required point by moving the top piston down.

The refractive index measurements of compressed liquid
carbonyl sulfide were determined at 273.2, 288.2, 303.2, 323.2, 343.2,
and 363.2 K from the vapor pressure to about 20 684 kPa. In addition,
refractive index measurements of carbonyl sulfide in the vapor phase
were made at 273.2, 323.2, and 383.2 K in order to estimate the molar
refractivities, R_{LL}, by using the volumetric data obtained from the
Burnett apparatus.

Carbonyl sulfide used for the refractive index measurements
was the same as that used for the Burnett experiments and had a
purity of 99.7 mole percent in the liquid phase.

C. Experimental Results and Discussion

The pertinent optical data (angles γ and δ) required for
determining the refractive indices of carbonyl sulfide in both the vapor
and liquid phases were measured at 273.2, 323.2, 383.2 K and 273.2,
288.2, 303.2, 323.2, 343.2, 363.2 K, respectively, at pressures
ranging from the vapor pressure to 20 700 kPa. The refractive indices
of carbonyl sulfide at these isotherms were calculated by using
Equation (28). The results are presented in both Tables F-1 through
F-7 of Appendix F. Figures 14 and 15 show the refractive indices of
carbonyl sulfide in the gaseous fluid region and in the dense
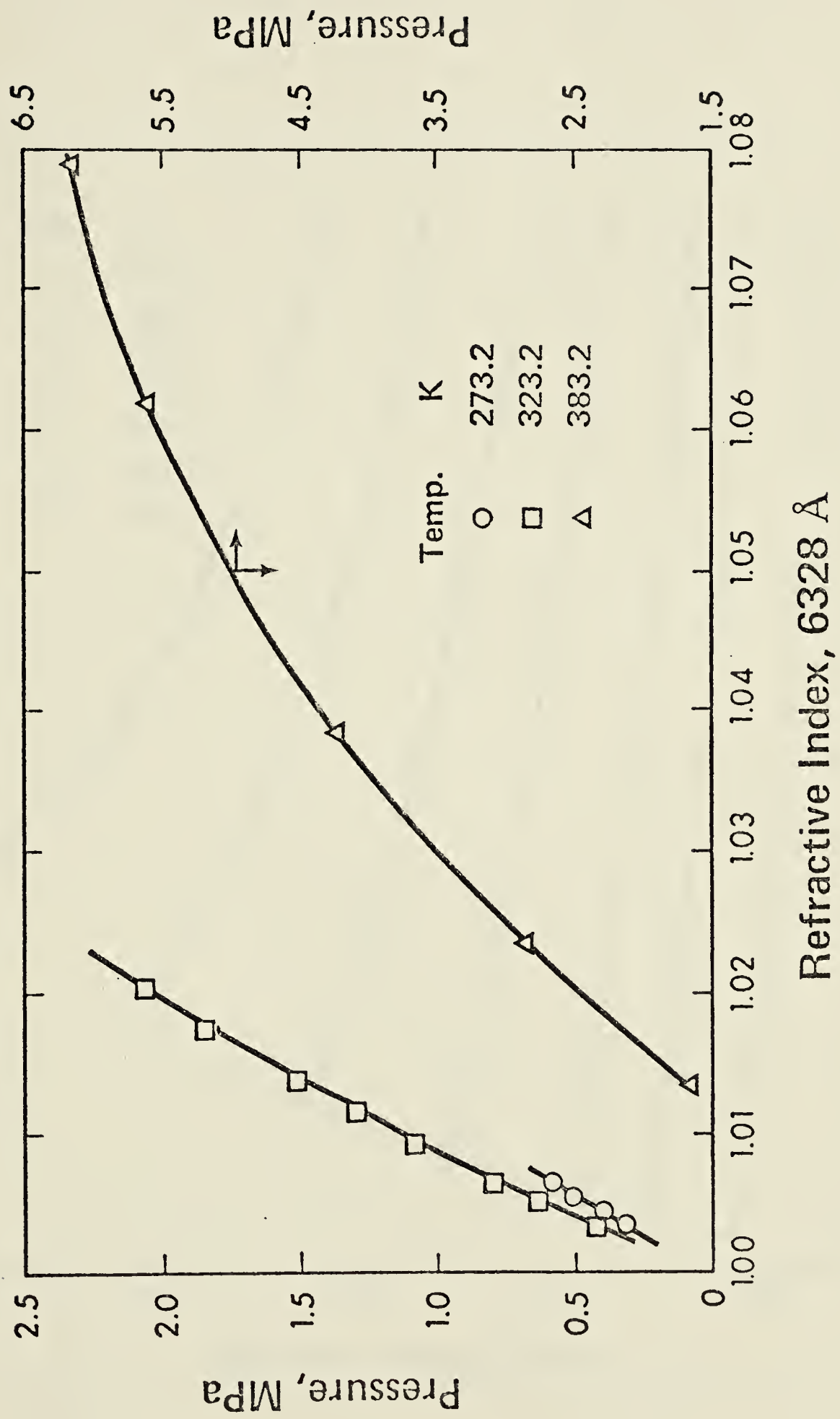
FIGURE 14. THE REFRACTIVE INDICES OF CARBONYL SULFIDE IN THE GASEOUS FLUID REGION
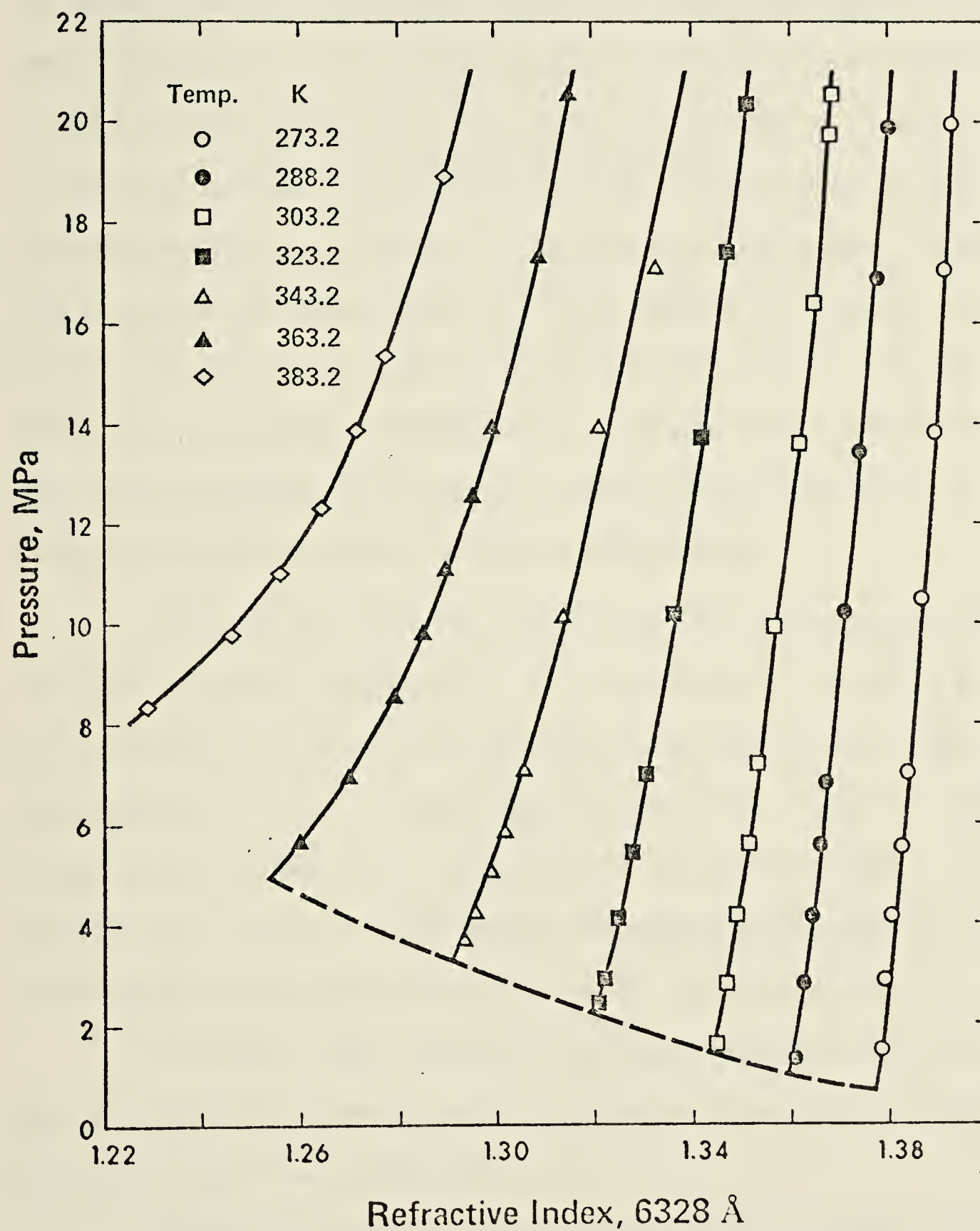
FIGURE 15. THE REFRACTIVE INDICES OF CARBONYL SULFIDE IN THE
DENSE FLUID REGION

fluid region, respectively.

The refractive indices of carbonyl sulfide which were measured in the vapor phase at 273.2, 323,2, and 383.2 K were used with the density determinations made using the Burnett equipment at the same temperatures to calculate the molal refractives from Equation (4). It had been intended to plot these molal refractivities as a function of pressure in order to establish the zero-pressure value at each temperature and also to establish the pressure coefficient. However, this procedure was unsuccessful at 273.2 and 323.2 K because the pressure interval over which the volumetric data existed was too narrow, and there was too much scatter in the calculated molal refractivities. This resulted because this region was one of maximum uncertainty in both the refractive index and density measurements.

In order to avoid this difficulty, the following procedure was used. Firstly, the densities of carbonyl sulfide at 383.2 K and up to pressures of 20 700 kPa were calculated using the Peng-Robinson (38) equation of state. These values agreed within about one percent of the Burnett measurements, and therefore it was felt that the densities of carbonyl sulfide in the compressed liquid region could be calculated with confidence at the lower two temperatures.

Secondly, these calculated and experimental values were used to establish the molal refractivities as a function of pressure at each of the three temperatures.

Finally, the molar refractivities at zero pressure and the pressure coefficients were determined as a function of temperature by fitting the quadratic equations at 273.2, 323.2, and 383.2 K isotherms, respectively, as follow :

$$R_{LL}^{o} = 33.4474 - 12.1833 \times 10^{-2}T + 18.5994 \times 10^{-5}T^2 \qquad (32)$$

$$m = 3.0005 \times 10^{-4} + 1.14803 \times 10^{-6}T - 1.04708 \times 10^{-9}T^2 \qquad (33)$$

where R_{LL}^{o} in $m^3/kmol$, m is in kPa^{-1}, and T is in K.

The molar refractivities at zero pressure and the corresponding pressure coefficients for the other 288.2, 303.2, 343.2, and 363.2 K isotherms were estimated by using Equations (32) and (33). The results of the estimated molar refractivities at zero pressure and the pressure coefficients are summarized in the following Table 8.

TABLE 8

CARBONYL SULFIDE ESTIMATED MOLAR REFRACTIVITIES AT ZERO

PRESSURE AND PRESSURE COEFFICIENTS

Isotherm (K)	R_{LL}^{o} (m^3/ kmol)	$m \times 10^5$ (kPa^{-1})
273.2	0.0141	-0.646
288.2	0.0138	-0.562
303.2	0.0136	-0.482
323.2	0.0135	-0.384
343.2	0.0135	-0.294
363.2	0.0137	-0.212
383.2	0.0141	-0.139

These R_{LL}^{o} and m values for the corresponding isotherms are also given in Appendix F.

Finally, Equation (31) was used to calculate the densities of carbonyl sulfide in the vapor and liquid phases at the prementioned isotherms and the pressure range studied. The results are summarized in Tables F-1 through F-7 of Appendix F.

VI - PREDICTED PROPERTIES

Several equations of state have been successfully used to predict the volumetric and vapor pressure data of pure hydrocarbon and non-hydrocarbon fluids as well as their mixtures. Hence, using the pertinent experimental data of carbonyl sulfide together with a well-known equation of state, one may predict the volumetric and vapor pressure data of carbonyl sulfide. Consequently, it was decided to use the Benedict-Webb-Rubin (39) equation of state as an example of a multi-constant equation, and the Peng-Robinson (38) equation of state as an example of a cubic equation in this study. A comparison of the experimental and the predicted data establishes the applicability of these equations of state to the behavior of carbonyl sulfide.

A. Method of Prediction

A-1. The Benedict-Webb-Rubin Equation of State

The Benedict-Webb-Rubin (BWR) equation of state, originally introduced in 1940 (39), has been widely used to predict the P-V-T properties as well as the thermodynamic properties of pure fluids and mixtures. The BWR equation of state has eight constants, and can be written as follows:

$$P = RT\rho + (B_o RT - A_o - C_o/T^2)\, \rho^2 + (bRT-a)\, \rho^3 + a\alpha\rho^6$$
$$+ c\, \rho^3/T^2\, (1+ \gamma\rho^2)\, e^{-\gamma\rho^2} \tag{34}$$

where B_o, A_o, C_o, b, a, α, c, and γ are constants.

Bishnoi and Robinson (40, 41) evaluated the BWR coefficients for some hydrocarbons and non-hydrocarbons using a nonlinear least squares technique applied to Equation (35). They obtained the

constants by simultaneously using P-V-T and vapor pressure data to minimize the error in density and in fugacities in the vapor and liquid phases along the vapor pressure curve. Their objective function

$$S = \sum_{i=1}^{M} \left[\frac{v_{ei} - v_{ki}}{v_{ei}} \right]^2 + W \sum_{j=1}^{M} \left[\frac{f_j^G - f_j^L}{f_j^G} \right]^2 \tag{35}$$

was used to determine the set of coefficients. The volume v_k is calculated from Equation (34) by a trial and error method, and the gas and liquid phase fugacities at the saturation points are calculated from Equation (36).

$$RT \ln f = RT \ln (PRT) + 2 \rho (B_o RT - A_o - \frac{C_o}{T^2})$$

$$+ 3 \rho (bRT - a)/2 + 6 a\alpha \rho^5/5$$

$$+ \frac{c\rho^2}{T^2} \frac{1 - e^{-\gamma\rho^2}}{\gamma\rho^2} + \frac{e^{-\gamma\rho^2}}{2} + \gamma\rho^2 e^{-\gamma\rho^2} \tag{36}$$

The weighting factor, W, (Equation (35)) is arbitrarily assigned to the set of vapor pressure data which is based on the relative amount of quality of P-V-T and vapor pressure data.

A-2. Peng-Robinson Equation of State

Recently, Peng and Robinson (38) proposed a two-constant equation of state in the following form:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \tag{37}$$

where the constants a and b at the critical point are

$$a(T_c) = 0.45724 \; \frac{R^2 T_c^2}{P_c} \tag{38}$$

$$b(T_c) = 0.07780 \; \frac{R T_c}{P_c} \tag{39}$$

At temperatures other than the critical, the constants of Peng-Robinson (PR) equation of state can be given as:

$$a(T) = a(T_c) \cdot \alpha \; (T_r, \; \omega) \tag{40}$$

$$b(T) = b(T_c) \tag{41}$$

where $\alpha (T_r, \; \omega)$ is a dimensionless function of reduced temperature and acentric factor and equals unity at the critical point.

For all substances examined the relationship between α and T_r can be linearized by the following equation:

$$\alpha^{\frac{1}{2}} = 1 + k \; (1 - T_r^{\frac{1}{2}}) \tag{42}$$

where k is a constant characteristic of each substance. The constant k for some hydrocarbons and non-hydrocarbons has been correlated by Peng and Robinson against the acentric factor. The resulting equation is

$$k = 0.37464 + 1.54226 \; \omega - 0.26992 \; \omega^2 \tag{43}$$

Therefore, in order to use the Peng and Robinson equation of state to predict the properties of pure substances, one should have the critical temperature, the critical pressure, and the acentric factor of the substance studied.

B. Results and Discussion

The constants in BWR equation of state were estimated by a

nonlinear least squares fit as suggested by Bishnoi (42) using the

experimental volumetric data obtained in Sections III and V and the

vapor pressure data obtained in Section IV. The constants were found

to be as:

$$B_o = 4.7557557 \times 10^{-2} \qquad a = 0.13032146$$

$$A_o = 5.4474307 \qquad \alpha = 2.8600401 \times 10^{-4}$$

$$C_o = 1.8451976 \times 10^{-5} \qquad c = 2.6678930 \times 10^{-6}$$

$$b = 8.1715191 \times 10^{-3} \qquad \gamma = 1.2194047 \times 10^{-2}$$

where the basic units in the constants are in atmospheres, degrees

Kelvin, and liters/mol.

The BWR equation of state with these estimated constants was

used to calculate the molar volumes, the compressibility factors in

both the vapor and liquid phase regions, and the molar volumes of

carbonyl sulfide in the saturated vapor and liquid phase region at the

range studied in this work. The results are presented in Tables G-1,

G-2, and G-3 of Appendix G, respectively.

The same properties of carbonyl sulfide including the vapor

pressures were predicted also using the Peng-Robinson equation of state,

the experimental critical temperature, critical pressure, and the

acentric factor calculated in this work. The results are presented

also in Tables G-1, G-2, and G-3 of Appendix G, respectively.

Two comparisons, one of the PR equation of state to the BWR

equation of state, and the other of the experimental results obtained in

this work to the values obtained by these equations may be summarized in

the following Table 9.

TABLE 9

THE COMPARISONS OF AVERAGE ABSOLUTE PERCENT DIFFERENCES FOR RESULTS

OBTAINED BY THE BWR AND PR EQUATIONS OF STATE, AND THIS WORK

Data Sets Used	$\dfrac{V_{BWR}-V_{PR}}{V_{BWR}} \cdot 10^2$	$\dfrac{V_{EX}-V_{PR}}{V_{EX}} \cdot 10^2$	$\dfrac{V_{EX}-V_{BWR}}{V_{EX}} \cdot 10^2$
Vapor	1.32	0.95	1.15
Liquid	3.80	3.66	4.83
Vapor + Liquid	2.49	2.23	2.88
Saturated Vapor	4.77		
Saturated Liquid	3.94		

VII - CONCLUSIONS

A. Volumetric Properties

Experimental volumetric data for carbonyl sulfide in the single phase region along the 273.2 and 323.2 K isotherms and the 383.2 K isotherm were obtained by using a Burnett apparatus at pressures up to the vapor pressure of carbonyl sulfide and to about 49 700 kPa, respectively.

B. Vapor Pressure and Critical Properties

Using a high-pressure constant-volume windowed liquid-level gauge, vapor pressure data for carbonyl sulfide were observed at temperatures ranging from 264.5 K to the critical point. The critical temperature, pressure, and volume of carbonyl sulfide were determined to be 378.8 K, 6349 kPa, and 0.135 m^3/kmol, respectively. The acentric factor for carbonyl sulfide was calculated according to Pitzer's definition and was found to be 0.096. The critical compressibility factor was calculated to be 0.272.

C. Refractive Index Measurements

The refractive indices of carbonyl sulfide along the 273.2, 288.2, 303.2, 343.2, 363.2, and 383.2 K isotherms were obtained using a helium - neon laser and an autocollimating telescope mounted on a windowed cell at pressures ranging from the vapor pressure to approximately 20 700 kPa.

D. Predicted Properties

The experimental and calculated volumetric data together with the vapor pressure data were used to obtain a set of parameters

for the Benedict-Webb-Rubin equation of state. They were as follows:

$$B_O = 4.7557557 \times 10^{-2} \qquad a = 0.13032146$$

$$A_O = 5.4474307 \qquad \alpha = 2.8600401 \times 10^{-4}$$

$$C_O = 1.8451976 \times 10^{-5} \qquad c = 2.6678930 \times 10^{-6}$$

$$b = 8.1715191 \times 10^{-3} \qquad \gamma = 1.2194047 \times 10^{-2}$$

where the basic units in the parameters are in atmospheres, degrees Kelvin, and liters/mol.

The critical pressure, critical temperature and acentric factor were used in the Peng-Robinson cubic equation of state to predict the volumetric behavior of carbonyl sulfide from 273.2 to 383.2 K at pressures from 160 to 49 700 kPa.

The results obtained using the cubic equation compared favorably with the results for the Benedict-Webb-Rubin equation, and both agreed within about one percent of the experimental values in the gaseous region. In the compressed liquid region, the results from the Benedict-Webb-Rubin equation differed from the experimental by 3.7 percent, and the results from the Peng-Robinson equation differed by 4.8 percent.

NOMENCLATURE

a, b	Coefficients of the PR equation of state
a, b	Inner and outer radius of the vessels in Equation (11)
A, B, C, D, E	Constants in Equation (3)
A_o, B_o, C_o, a, b, c, α, γ	Coefficients of the BWR equation of state
$\overset{o}{A}$	Angstrom
B, C, D, B', C', D'	Coefficients of the virial equation of state
B, C	Second and third virial refractivity coefficients
C	Centigrade
E	Modulus of elasticity in Equation (11)
f	fugacity
F	Fahrenheit
k	Defined in Equation (43)
K	Kelvin
m	Pressure coefficient in Equation (30)
n	Number of moles or refractive index
N	Burnett cell constant
P	Pressure
R	Universal Gas Constant
R_{LL}	Lorentz-Lorenz refractivity
R_{LL}^o	Molar refractivity at zero pressure
S	Defined in Equation (36)
t, T	Temperature
v	Volume
Z	Compressibility factor

Greek Letters

α	Coefficient in Equation (13) or dimensionless function in Equation (43)
β	Angle of refraction in the window
γ	Minimum deviation angle measured by autocollimation
δ	Prism angle
ρ	Density
ω	Acentric factor

Subscripts

o	Value as P approaches zero
1, 2	Number of expansion in Burnett experiment or designation of volume vessels in Burnett cell
j	Any expansion in Burnett experiment
c	Refers to critical state
R	Refers to reduced state
e	Experimental value
i, j	Refers to state i or j
k	Calculated value

Superscripts

j	jth expansion
'	denotes prime
o	denotes degree
G	denotes gas phase
L	denotes liquid phase

REFERENCES

[1] Kemp, J.D., and Giauque, W.F., J. Am. Chem. Soc., 59, 79 (1937).

[2] Partington, J.R., and Neville, H.H., J. Phys. Colloid Chem., 55, 1550 (1951).

[3] Than, C., Ann. Suppl., 5, 237 (1867).

[4] Ferm, R.J., Chem. Rev., 57, 621 (1957).

[5] Miranda, R.D., "The Equilibrium Phase Properties of the Carbonyl Sulfide-Propane System", M.Sc. Thesis in Chemical Engineering, University of Alberta, Edmonton (1974).

[6] Stock, A., and Kuss, E., Ber. Deut. Chem. Gesell., 50, 159 (1917).

[7] Pearson, T.G., Robinson, P.L., and Trotter, J., J. Chem. Soc., 600 (1932).

[8] Hempel, W., Z. angew. Chem., 14 (35), 865 (1901).

[9] Ilosvay, M., Bull. Soc. Chim., 37, 294 (1882).

[10] Honig, R.E., and Hook, H.O., R.C.A. Review, 21, 360 (1960).

[11] Matheson Gas Products Company, 1973 Publication on COS.

[12] Kobe, K.A., and Lynn, R.E., Jr., Chem. Rev., 52, 117 (1953).

[13] Lydersen, A.L., Estimation of Critical Properties of Organic Compounds, Coll. Eng., Univ. Wisconsin, Eng. Exp. Sta. Rept. 3, Madison, Wis., April, 1955.

[14] Francis, A.W., J. Chem. Eng. Data, 5, 534 (1960).

[15] Wong, L.Y., and Anderson, A., J. Optical Soc. Am., 62, 219 (1972).

[16] Nelson, K.H., Veal, D., and Heinrich, B.J., Petrol. Ref. 34 (7), 155 (1955).

[17] Freise, F.W., Concrete Constr. Eng., 28, 299 (1933).

[18] Cross, P.C., J. Chem. Phys., 3, 825 (1935).

[19] International Critical Tables, McGraw-Hill Publishing Company, Inc., New York, III, 231 (1928).

[20] McBride, B.J., and Gordon, S., J. Chem. Phys., 35, 2198 (1961).

[21] Zandler, M.E., Watson, J.A., Jr., and Eyring, H., J. Phys. Chem., 72, 2730 (1968).

[22] Burnett, E.S., J. Appl. Mechanics, 58, A136-40 (1936).

[23] Canfield, F.B., Leland, T.W., and Kobayashi, R., Advan. Cryog. Eng., 8, 146, (1963).

[24] Silberberg, I.H., Kobe, K.A., and McKetta, J.J., J. Chem. Eng. Data, 4, 314 (1959).

[25] Ku, P.S., and Dodge, B.F., J. Chem. Eng. Data, 12, 158 (1967).

[26] Mueller, W.H., Leland, T.W., Jr., and Kobayashi, R., A.I.Ch.E. J., 7, 267 (1961).

[27] Robinson, D.B., Hamaliuk, G.P., Krishnan, T.R., and Bishnoi, P.R., J. Chem. Eng. Data, 20, 153 (1975).

[28] Wu, B.J., Robinson, D.B., Ng. H.J., J. Chem. Thermodyn., 8, 461 (1976).

[29] Wu, B.J., "Hydrates in the Methane-Isobutane System and in Liquified Light Hydrocarbon", M.Sc. Thesis in Chemical Engineering, University of Alberta, Edmonton (1974).

[30] Rowlinson, J.S., "Liquids and Liquid Mixtures", 2nd ed., p. 76, Butterworths, London, 1969.

[31] Kudchadker, A.P., Alani, G.H., and Zwolinski, B.J., Chem. Rev., 68, 659 (1968).

[32] Newton, I., Opticks, book II, 245 (1704)

[33] Besserer, G.J., "The Use of Refractive Index Measurements in High Pressure Vapor-Liquid Equilibrium Studies", Ph.D. Thesis in Chemical Engineering, University of Alberta, Edmonton (1972).

[34] Lorentz, H., Wied. Ann., 9, 641 (1880).

[35] Lorenz, L., Wied. Ann., 11, 70 (1880).

[36] Buckingham, A.D., and Pople, J.A., Disc. of Faraday Soc., 22, 17 (1956).

[37] Besserer, G.J., and Robinson, D.B., Can. J. Chem. Eng., 49, 651 (1971).

[38] Peng, D.Y., and Robinson, D.B., Ind. Eng. Chem., Fundam., 15, 59 (1976).

[39] Benedict, M., Webb, G.B., and Rubin, L.C., J. Chem. Phys., 8, 334 (1940).

[40] Bishnoi, P.R., and Robinson, D.B., Hydrocarbon Processing,
      51, (11), 152 (1972).

[41] Bishnoi, P.R., Miranda, R.D., and Robinson, D.B., Hydrocarbon
      Processing, 53, (11), 197 (1974).

[42] Bishnoi, P.R., "Experimental Heat Capacities of Carbon Dioxide -
      Methane Mixtures at Elevated Pressures and the Correlation
      of Volumetric and Thermal Properties", Ph.D. Thesis in
      Chemical Engineering, University of Alberta, Edmonton (1971).

APPENDIX A

PRESSURE MEASUREMENT

PART 1

Pressure Measurement Corrections for the Volumetric Data Obtained in the Burnett Experiments

The pressure exerted by the gas in the Burnett cell was measured by balancing pressures across a diaphragm in a differential pressure cell and by applying the appropriate corrections. The hydraulic oil in the dead-weight gauge was connected to the upper compartment of the differential pressure cell and the sample gas from the Burnett cell was connected to the lower compartment of the differential pressure cell. The diaphragm of the differential pressure cell is normally flexed by the imbalance of the applied pressures. This imbalance was relayed to a differential pressure indicator which indicated that the pressure in the gauge was either higher, lower than, or equal to, the pressure in the Burnett cell.

The total pressure, P, exerted by the gas in the Burnett cell can be written as:

$$P = P_G + P_B - P_H \qquad \text{(A1-1)}$$

where

P_G = the pressure exerted on the piston in the dead-weight gauge

P_B = barometric pressure acting on the piston

P_H = hydraulic oil head correction

The primary purpose of this Appendix is to show how each of these contributions to the total pressure was determined.

A1-1. Calculation of Gauge Pressure, P_G

The equation for calculating the pressure exerted by the gauge is given as follows:

$$P_G = \frac{(W+T)}{A_e} \frac{g}{g_s} \left(1 - \frac{\rho_a}{\rho_b}\right) \qquad (A1\text{-}2)$$

where

P_G = pressure exerted by the gauge as measured

W = weight load of the masses that were applied to the gauge

T = weight load for the piston assembly

    for high range = 0.78108 pounds (30 psi)

    for low range = 0.78106 pounds (6 psi)

A_e = effective area of piston

g = local gravity = 980.159 cm/sec^2

g_s = standard gravity = 980.665 cm/sec^2

ρ_a = density of air = 0.0012 g/ml.

ρ_b = density of brass = 8.4 g/ml.

Table A1-1 gives the tabulation of weights for Type 2400 HL Ruska Dead Weight Gauge, Serial No. 12436.

a. Correction for Change in Temperature

Variations in the indicated pressure resulting from changes in temperature arise from the expected change in effective area of piston, A_e. By substituting the difference in temperature from the reference temperature, and the thermal coefficient of area expansion in the relation

$$A_{o(t+\Delta t)} = A_{o(t=25°C)} (1+C\Delta t) \qquad (A1\text{-}3)$$

Table A1-1. Weight Tabulation (psi), Serial No. 12436

Weight Number	Pressure (psi)		Apparent Mass vs Brass Standards (pounds)
	High Range	Low Range	
A	1000	200	26.03551
B	1000	200	26.03571
C	1000	200	26.03615
D	1000	200	26.03602
E	1000	200	26.03600
F	1000	200	26.03579
G	1000	200	26.03598
H	1000	200	26.03518
I	1000	200	26.03592
J	1000	200	26.03503
K	1000	200	26.0560
L	500	100	13.01778
M	200	40	5.20711
N	200	40	5.20710
O	100	20	2.60361
P	50	10	1.30179
Q	20	4	0.520697
R	20	4	0.520723
S	10	2	0.260371
T	5	1	0.130173
U	2	0.4	0.052090
V	2	0.4	0.052087
W	1	0.2	0.026035
X	0.5	0.1	0.013016
	0.2	0.04	0.0051916
	0.2	0.04	0.0051965
	0.1	0.02	0.0025960
	0.05	0.01	0.0012925

where

$A_{o(t+\Delta t)}$ = area corrected to the working temperature

$A_{o(t=25°C)}$ = area of piston at zero psig and at reference

temperature of 25°C

for high range = 0.0260378 inch^2

for low range = 0.130222 inch^2

C = thermal coefficient

for high and low range = 1.5 x 10^{-5}/°C

Δt = difference between working temperature and

reference temperature

b. Correction for Elastic Distortions

If the change in effective area of the piston is proportional to the change in pressure, the area may be determined by substituting values for the pressure which is given by:

$$A_e = A_{o(t+\Delta t)}(1+bP) \tag{A1-4}$$

where A_e = effective area at pressure P

$A_{o(t+\Delta t)}$ = effective area at zero psig which is calculated by Equation (A1-3)

b = fractional change in area per unit change in pressure

for high and low range = -3.5 x 10^{-8}/psi

P = operating pressure.

The effective area A_e calculated by Equation (A1-4) should be used in Equation (A1-2).

A1-2.   Calculation of Barometric Pressure, P_B

The barometric pressure was determined with a Fortin-type barometer. The scale on the barometer could be read to 0.1 mm by means of a vernier. A thermometer was mounted near the middle of the barometer, and it served to determine the temperature of the mercury column.

A single equation incorporating a temperature correction, that holds true for ordinary room temperatures, was used to calculate the barometric pressure. The pressure P_B in psi is given by:

$$P_B = \left[13.5462 - 0.00245(t_c-20)\right] (1.45038 \times 10^{-5}) \, g \cdot h_c$$

$$= (1.96471 \times 10^{-4}) \left[1 - 1.81 \times 10^{-4} (t_c-20)\right] g \cdot h_c \qquad (A1-5)$$

where

h_c = measured height mercury in cm

t_c = temperature in °C

g = local gravity = 981.159 cm/sec^2

Equation (A-5) can be also given as follows:

$$P_B = 0.1927693 \left[1 - 1.81 \times 10^{-4} (t_c-20)\right] h_c \qquad (A1-6)$$

A1-3.   Hydraulic Oil head Correction, P_H

Owing to a height difference between the diaphragm of the differential pressure cell and the reference point of the dead-weight gauge, a correction has to be made to account for the hydraulic oil head. The formula used for hydraulic head correction is given as:

$$P_H = \rho (h_1 - h_2) \frac{g}{g_s} \qquad (A1-7)$$

where P_H = hydraulic oil head correction in psi

ρ = density of oil = 0.031 lbs/inch^3

h_1 = 2.7 inch

h_2 = 2.13 inch

g = local gravity

g_s = standard gravity

Hydraulic head correction, P_H, was calculated to be 0.017679 psi.

PART 2

Pressure Measurement Corrections for the Vapor Pressure Data Obtained in the Constant Volume Equilibrium Cell Experiments

The total pressure, P, exerted by the sample fluid in the constant volume equilibrium cell can be written as,

$$P = P_G + P_B - P_H - P_F \tag{A2-1}$$

where P_G = the pressure exerted on the piston in the dead-weight gauge

P_B = barometric pressure acting on the piston

P_H = hydraulic oil head correction

P_F = hydrostatic sample fluid head correction

The contribution of these pressure and corrections to the total pressure was described as below:

A2-1. Calculation of Gauge Pressure, P_G

The formula for calculating the pressure exerted by the gauge is given by the equation:

$$P_G = P_e + \frac{W}{A} (K) \frac{g}{g_s} \tag{A2-2}$$

where P_G = pressure exerted by the gauge as measured

P_e = pressure of empty weight at standard gravity

for high range = 30.00 psi

for low range = 6.00 psi

W = weight of dead weights, at standard gravity, in grams

A = effective area of piston

for high range = 0.026038 inch^2

$$\text{for low range} = 0.13023 \text{ inch}^2$$

K = conversion constant = 0.0022046 lbs/gram

g = local gravity = 981.159 cm/sec^2

g_s = standard gravity = 980.665 cm/sec^2

Table A2-1 gives the tabulation of weights for Type 2400 HL Ruska Dead Weight Gauge, Serial No. 8338.

a. Correction for Elastic Distortions

The application of pressure causes elastic distortions in the piston and cylinder, resulting in a change of effective area. As the pressure surrounds the piston and cylinder, the diameters are decreased, causing an increase of pressure. The formula for calculating corrections for the effect of elastic distortion is

$$P_E = P_G (1 - f_p P) \tag{A2-3}$$

where P_E = corrected pressure for elastic distortions

P_G = measured pressure calculated by Equation (A2-2)

f_p = fraction change of area per unit pressure

for high range = -4.2 x 10^{-8}/psi

for low range = -4.7 x 10^{-8}/psi

b. Correction for Change in Temperature

Rise in temperature results in a decrease of pressure exerted by the weights. The formula for calculating correct pressures for change in temperature is:

$$P_T = P_E \left[1 - f_t (t - 20) \right] \tag{A2-4}$$

Table A2-1. Weight Tabulation (psi), Serial No. 8338

Weight Number	Pressure (psi)		Weight (grams)
	High Range	Low Range	
A	1000	200	11810.7
B	1000	200	11810.8
C	1000	200	11810.8
D	1000	200	11810.8
E	1000	200	11810.8
F	1000	200	11810.8
G	1000	200	11810.8
H	1000	200	11810.8
I	1000	200	11810.8
J	1000	200	11810.8
K	1000	200	11810.8
L	500	100	5905.41
M	200	40	2362.16
N	200	40	2362.17
O	100	20	1181.11
P	50	10	590.55
Q	20	4	236.217
R	20	4	236.214
S	10	2	118.108
T	5	1	59.054
U	2	0.4	23.621
V	2	0.4	23.621
W	1	0.2	11.810
X	0.5	0.1	5.905
	0.2	0.04	2.357
	0.2	0.04	2.3592
	0.1	0.02	1.1786
	0.05	0.01	0.5868

where P_T = corrected pressure for change in temperature

          P_E = measured pressure calculated by Equation (A2-3)

          f_t = fractional change of effective area with temperature

              for high and low range = $2.4 \times 10^{-5}/°C$

          t   = temperature, °C

The pressure P_T which is calculated by using Equation (A2-4) should be used in Equation (A2-1) as P_G.

A2-2. Calculation of Barometric Pressure, P_B

Determination of the barometric pressure was the same as that used for the Burnett experiments which is Part 1 of the same Appendix A. The barometric pressure P_B in psi is given by:

$$P_B = 0.1927693 \left[1-1.81 \times 10^{-4} (t_c-20) \right] h_c \qquad \text{(A2-5)}$$

where t_c = temperature in °C

          h_c = measured height mercury in cm

A2-3. Hydraulic Oil Head Correction, P_H

The formula used for the hydraulic oil head correction is

$$P_H = \rho (h_1-h_2) \frac{g}{g_s} \qquad \text{(A2-6)}$$

where P_H = hydraulic oil head correction in psi

          ρ = density of oil = 0.031 lbs/inch^3

          h_1 = 5.25 inch

          h_2 = 4.25 inch

          g = local gravity

g_S = standard gravity

The value of P_H was found to be 0.030723 psi.

A2-4. Hydrostatic Sample Fluid Head Correction, P_F

Owing to the difference in the levels of the meniscus of vapor and liquid carbonyl sulfide in the constant volume equilibrium cell at any isotherm as compared to the reference point, a correction has to be made to account for the sample fluid head. The formula for the hydrostatic sample fluid head correction is given as:

$$P_F = \rho \left[(h + h_1) - h_2 \right] \frac{g}{g_S} \qquad \text{(A2-7)}$$

where P_F = hydrostatic sample fluid head correction in psi

           ρ^* = density of carbonyl sulfide at any isotherm and at the corresponding vapor pressure

           h = the liquid carbonyl sulfide level height difference between the reference plane and the meniscus of two phases.

           h_1 = 13.75 inch

           h_2 = 5.25 inch

* The density of carbonyl sulfide in the liquid region interpolated from the data of Partington and Neville (2).

APPENDIX B

VOLUMETRIC DATA OF CARBONYL SULFIDE

The volumetric properties as measured by using the Burnett apparatus are presented in Tables B-1 through B-3.

Table B-1. Burnett Cell Calibration Data with Helium.

Temp. (K)	Run No.	j	P_{j-1} (MPa)	$\dfrac{P_{j-1}}{P_j}$
273.2	1	1	13.943	1.5128
		2	9.2169	1.5014
		3	6.1387	1.4940
		4	4.1088	1.4888
		5	2.7599	1.4860
		6	1.8572	1.4834
		7	1.2520	1.4820
		8	0.84484	1.4810
		9	0.57046	1.4802
		10	0.38539	1.4797
		11	0.26045	......
323.2	1	1	16.144	1.5114
		2	10.681	1.5006
		3	7.1179	1.4933
		4	4.7666	1.4886
		5	3.2021	1.4853
		6	2.1559	1.4832
		7	1.4535	1.4815
		8	0.98110	1.4803
		9	0.66275	1.4799
		10	0.44785	1.4788
		11	0.30284	......

Table B-1. (Continued)

Temp. (K)	Run No.	j	P_{j-1} (MPa)	$\dfrac{P_{j-1}}{P_j}$
323.2	2	1	15.979	1.5109
		2	10.576	1.5004
		3	7.0484	1.4933
		4	4.7202	1.4885
		5	3.1711	1.4853
		6	2.1350	1.4831
		7	1.4395	1.4813
		8	0.97188	1.4804
		9	0.65650	1.4795
		10	0.44373	1.4790
		11	0.30003	......
383.2	1	1	14.958	1.5039
		2	9.9465	1.4953
		3	6.6520	1.4895
		4	4.4658	1.4865
		5	3.0043	1.4834
		6	2.0252	1.4811
		7	1.3674	......
383.2	2	1	10.736	1.4966
		2	7.1734	1.4908
		3	4.8119	1.4857
		4	3.2387	1.4838
		5	2.1828	1.4820
		6	1.4729	1.4816
		7	0.99410	1.4792
		8	0.67207	......

Table B-1. (Continued)

Temp. (K)	Run No.	j	P_{j-1} (MPa)	$\dfrac{P_{j-1}}{P_j}$
383.2	3	1	3.6697	1.4839
		2	2.4731	1.4828
		3	1.6679	1.4811
		4	1.1261	1.4797
		5	0.76102	1.4718
		6	0.51706	1.4792
		7	0.34957	......

Table B-2. Experimental Carbonyl Sulfide Data for
Estimation of the Run Constant (P_o/Z_o)

Temp. (K)	Run No.	j	P_j (MPa)	N_j	$P_j N_j^j$ (MPa)
273.2	1	1	0.44708	1.4789	0.66119
		2	0.30982	1.4789	0.67763
		3	0.21288	1.4789	0.68860
273.2	2	1	0.38198	1.4789	0.56491
		2	0.26354	1.4789	0.57640
		3	0.18053	1.4789	0.58396
323.2	1	1	1.7154	1.4785	2.5337
		2	1.2389	1.4785	2.7080
		3	0.87445	1.4785	2.8260
		4	0.60839	1.4785	2.9070
		5	0.41941	1.4785	2.9629
		6	0.28741	1.4785	3.0018
		7	0.19671	1.4785	3.0292
323.2	2	1	1.9901	1.4785	2.1594
		2	1.4605	1.4785	2.2747
		3	1.0407	1.4785	2.3535
		4	0.50381	1.4785	2.4073
		5	0.34593	1.4785	2.4438
		6	0.23634	1.4785	2.4684
		7	0.16104	1.4785	2.4867

Table B-2. (Continued)

Temp. (K)	Run No.	j	P_j (MPa)	N_j	$P_j N_j^j$ (MPa)
		4	0.50381	1.4785	2.4073
		5	0.34593	1.4785	2.4438
		6	0.23634	1.4785	2.4684
		7	0.16104	1.4785	2.4867
383.2	1	1	2.3692	1.4781	3.5020
		2	1.6819	1.4781	3.6747
		3	1.1751	1.4781	3.7947
		4	0.81364	1.4781	3.8838
		5	0.55889	1.4781	3.9434
		6	0.38268	1.4781	3.9910
		7	0.26144	1.4781	4.0303
383.2	2	1	8.1732	1.4780	12.072
		2	6.8628	1.4781	14.993
		3	6.5899	1.4781	21.282
		4	5.8866	1.4781	28.098
		5	4.8112	1.4781	33.943
		6	3.7029	1.4781	38.615
		7	2.7285	1.4781	42.057
		8	1.9537	1.4781	44.512
		9	1.3738	1.4781	46.268
		10	0.95436	1.4781	47.509
		11	0.65745	1.4781	48.378
		12	0.45019	1.4781	48.966
		13	0.30904	1.4781	49.685
		14	0.21085	1.4781	50.108

Table B-2. (Continued)

Temp. (K)	Run No.	j	P_j (MPa)	N_j	$P_j N_j^j$ (MPa)
383.2	3	1	7.1192	1.4780	10.521
		2	6.7783	1.4781	14.809
		3	6.3591	1.4781	20.536
		4	5.4840	1.4781	26.176
		5	4.3717	1.4781	30.843
		6	3.2987	1.4781	34.399
		7	2.4025	1.4781	37.033
		8	1.7068	1.4781	38.889
		9	1.1936	1.4781	40.198
		10	0.82719	1.4781	41.179
		11	0.56969	1.4781	41.920
		12	0.38986	1.4781	42.404
		13	0.26678	1.4781	42.891
383.2	4	1	7.5485	1.4780	11.152
		2	6.8242	1.4781	14.909
		3	6.5152	1.4781	21.040
		4	5.7557	1.4781	27.474
		5	4.6737	1.4781	32.974
		6	3.5666	1.4781	37.193
		7	2.6195	1.4781	40.377
		8	1.8709	1.4781	42.627
		9	1.3122	1.4781	44.194
		10	0.9113	1.4781	45.357
		11	0.62731	1.4781	46.160
		12	0.43055	1.4781	46.830
		13	0.29445	1.4781	47.339

Table B-3. Experimental and Calculated Carbonyl Sulfide Data

Temp. (K)	No.	j	P_j (MPa)	Z_j	$V_j(Z_j-1)$ (m^3/kmol)	$1/V_j$ (kmol/m^3)
273.2	1	0	0.63595	0.89107	-0.34663	0.31423
		1	0.44708	0.92644	-0.34619	0.21248
		2	0.30982	0.94947	-0.35172	0.14367
		3	0.21288	0.94684	-0.36192	0.097148
273.2	2	0	0.54728	0.91035	-0.33865	0.26469
		1	0.38198	0.93970	-0.33694	0.17898
		2	0.26354	0.95881	-0.34036	0.12102
		3	0.18053	0.97137	-0.34985	0.081831
323.2	1	0	2.2710	0.73562	-0.23010	1.14896
		1	1.7154	0.82153	-0.22965	0.77714
		2	1.2389	0.87718	-0.23368	0.52564
		3	0.87445	0.91539	-0.23798	0.35553
		4	0.60839	0.94161	-0.24280	0.24047
		5	0.41941	0.95973	-0.24762	0.16264
		6	0.28741	0.97234	-0.25143	0.11001
		7	0.19671	0.98123	-0.25234	0.074405
323.2	2	0	1.9901	0.78860	-0.22507	0.93920
		1	1.4605	0.85568	-0.22718	0.63525
		2	1.0407	0.90140	-0.22948	0.42967
		3	0.72824	0.93260	-0.23191	0.29062
		4	0.50381	0.95391	-0.23447	0.19656
		5	0.34593	0.96837	-0.23791	0.13295
		6	0.23634	0.97816	-0.24293	0.089923
		7	0.16104	0.98541	-0.23991	0.060821

Table B-3. (Continued)

Temp. (K)	Run No.	j	P_j (MPa)	Z_j	$V_j (Z_j-1)$ (m^3/kmol)	$1/V_j$ (kmol/m^3)
383.2	1	0	3.2562	0.79721	-0.15817	1.28208
		1	2.3692	0.85738	-0.16443	0.86739
		2	1.6819	0.89966	-0.17098	0.58683
		3	1.1751	0.92906	-0.17869	0.39701
		4	0.81364	0.95087	-0.18292	0.26859
		5	0.55889	0.96545	-0.19015	0.18171
		6	0.38268	0.97712	-0.18616	0.12293
		7	0.26144	0.98673	-0.15955	0.083168
383.2	2	0	49.669	0.98701	-0.00082184	15.796
		1	8.1732	0.23988	-0.093504	10.695
		2	6.8628	0.29795	-0.097102	7.2301
		3	6.5899	0.42290	-0.11799	4.8912
		4	5.8866	0.55837	-0.13346	3.3092
		5	4.8112	0.67452	-0.14537	2.2389
		6	3.7029	0.76734	-0.15360	1.5147
		7	2.7285	0.83576	-0.16027	1.0248
		8	1.9537	0.88454	-0.16654	0.69329
		9	1.3738	0.91943	-0.17178	0.46902
		10	0.95436	0.94409	-0.17621	0.31731
		11	0.65745	0.96135	-0.18003	0.21466
		12	0.45019	0.97304	-0.18565	0.14523
		13	0.30904	0.98733	-0.12898	0.098249
		14	0.21085	0.99573	-0.06421	0.066468

Table B-3. (Continued

Temp. (K)	Run No.	j	P_j (MPa)	Z_j	$V_j (Z_j-1)$ $(m^3/ kmol)$	$1/V_j$ $(kmol/m^3)$
383.2	3	0	17.940	0.41322	-0.043058	13.627
		1	7.1192	0.24233	-0.082164	9.2214
		2	6.7783	0.34111	-0.10563	6.2374
		3	6.3591	0.47302	-0.12488	4.2199
		4	5.4840	0.60294	-0.13908	2.8550
		5	4.3717	0.71042	-0.14992	1.9316
		6	3.2987	0.79233	-0.15891	1.3068
		7	2.4025	0.85299	-0.16628	0.88410
		8	1.7068	0.89576	-0.17429	0.59812
		9	1.1936	0.92591	-0.18309	0.40464
		10	0.82719	0.94849	-0.18815	0.27375
		11	0.56969	0.96557	-0.18593	0.18520
		12	0.38986	0.97672	-0.18583	0.12529
		13	0.26678	0.98794	-0.14233	0.084763
383.2	4	0	32.962	0.68645	-0.020803	15.072
		1	7.5485	0.23226	-0.075256	10.202
		2	6.8242	0.31050	-0.099946	6.8987
		3	6.5152	0.43818	-0.12038	4.6672
		4	5.7557	0.57216	-0.13549	3.1576
		5	4.6737	0.68671	-0.14665	2.1363
		6	3.5666	0.77458	-0.15596	1.4453
		7	2.6195	0.84090	-0.16271	0.97782
		8	1.8709	0.88775	-0.16968	0.66152
		9	1.3122	0.92037	-0.17793	0.44754
		10	0.91113	0.94461	-0.18296	0.30277
		11	0.62731	0.96132	-0.18886	0.20483
		12	0.43055	0.97527	-0.17846	0.13857
		13	0.29445	0.98588	-0.15060	0.093748

APPENDIX C

ERROR ANALYSIS IN CALCULATING OF COMPRESSIBILITY FACTORS

OF CARBONYL SULFIDE

The calculation of the maximum percent error in the compressibility factors follows a procedure similar to that used by Canfield et al. (23).

The compressibility factors of carbonyl sulfide using the Burnett apparatus are calculated by:

$$Z_i = \left(\frac{P_o}{Z_o}\right)^{-1} P_j N_j^j \tag{C-1}$$

or

$$Z_j = \frac{P_j N_1 N_2 \ldots \ldots N_j}{P_o/Z_o} \tag{C-2}$$

Total differentiation of Equation (C-2) at constant temperature, and replacement of the differentials by delta quantities, gives for the error in Z_j,

$$\Delta Z_j = \frac{N_j^j \Delta P_j + P_j N^j (\Delta N_1/N_1 + \Delta N_2/N_2 + \ldots + \Delta N_j/N_j) - Z_j \Delta(P_o/Z_o)}{P_o/Z_o} \tag{C-3}$$

where $N_1 N_2 \ldots \ldots N_j \simeq N_j^j$. At this point, it is imperative to recognize that the error in P_o/Z_o, $\Delta[P_o/Z_o]$, is closely related to the errors in the cell constants N_j and the errors in the pressure P_j, since

$$P_o/Z_o = \lim_{P_j \to 0} P_j N_1 N_2 \ldots \ldots N_j \tag{C-4}$$

From Equation (C-4) it can be seen that there are two sources of error in the value of P_o/Z_o, namely:

1) Those arising from actual errors in the values of $P_j N_1 N_2 \ldots \ldots N_j$ at low pressure.

2) Those due to the extrapolation of P_j N_1 N_2 ...N_j to zero pressure.

It is convenient to specify these errors as being due to (1) the error in P_j N_1 N_2.... N_j at $j = m =$ total number of expansions for a particular run, and (2) the error introduced in extrapolating the experimental values of P_j N_1 N_2....N_j from $j = m$ to zero pressure. The first part of the error is then directly obtainable from (C-4), and the second part can be estimated by statistical methods or a plot of P_j N_1 N_2....N_j versus P_j. From Equation (C-4)

$$\Delta(P_0/Z_0) = N_m^m \Delta P_m + P_m N_m^m (\Delta N_1/N_1 + \Delta N_2/N_2 +....+ \Delta N_m/N_m) + E \qquad (C-5)$$

where E is the error introduced in P_0/Z_0 due to uncertainties in extrapolating the values of P_j N_1 N_2 ....N_j from P_m to zero pressure. Substitution of Equation (C-5) into Equation (C-3) with the approximations that $Z_m = 1$ and P_j $N_j^j = Z_j$ P_0/Z_0 gives

$$(\Delta Z_j)_p = \frac{N_j^j \Delta P_j - Z_j N_m^m \Delta P_m}{P_0/Z_0} - Z_j \left[\frac{\Delta N_{j+1}}{N_{j+1}} + ... + \frac{\Delta N_m}{N_m} \right]$$

$$\pm \frac{Z_j E}{P_0/Z_0} \qquad (C-6)$$

The error in the absolute determination of temperature must also be considered. The contribution to the error in the compressibility factor due to an error in temperature is given by:

$$(\Delta Z_j)_T = (\frac{\partial Z}{\partial T})_{P_j} \Delta T \qquad (C-7)$$

The total error in the compressibility factor is then the sum of Equations (C-6) and (C-7).

$$\Delta Z_j = (\Delta Z_j)_T + (\Delta Z_j)_p \tag{C-8}$$

Equation (C-8) serves to establish the maximum error limits for the experimental compressibility factors. Hence the expected maximum errors in compressibility factors at some pressures for each isotherm may be summarized in the following Table (C-1).

Table C-1. Estimated Maximum Errors in Compressibility Factors

Isotherm K	j	P_j (MPa)	Z_j	$(\Delta Z_j)_P 10^2$	$(\Delta Z_j)_T 10^2$	% Relative Error
273.2	3	0.18053	0.97137	1.0103	0.01464	1.06
	2	0.30982	0.94947	1.0645	0.01464	1.13
	0	0.63595	0.89107	1.0185	0.01464	1.16
323.2	7	0.16104	0.98541	0.11804	0.01238	0.13
	4	0.50381	0.95391	0.14140	0.01238	0.16
	0	2.2710	0.73562	0.10243	0.01238	0.15
	0	1.9901	0.78860	0.15847	0.01238	0.21
383.2	14	0.21085	0.99573	0.16524	0.01044	0.18
	9	1.1936	0.92591	0.25749	0.01044	0.29
	7	2.6195	0.84090	0.40563	0.01044	0.48
	0	49.669	0.98701	0.54063	0.01044	0.56
	0	32.962	0.68645	0.58227	0.01044	0.86

APPENDIX D

VOLUMETRIC MEASUREMENTS

The pertinent data on the volumetric measurements for the critical properties of carbonyl sulfide may be summarized as below:

A. The Volume of the Constant Equilibrium Cell

The volume of the cell was determined by using mercury. The details of the volume measurements may be given as follows:

Temperature = 296.6 K

Density of Mercury[*] = 13.5370 g/ml

Test No.	The Weight of Mercury (g)	The Volume of the Cell (ml)
1	1011.1155	74.693
2	1010.9051	74.677
3	1011.5817	74.727

The average volume of the cell = 74.704 ml.

[*]Perry, J.H., "Chemical Engineering Handbook", 4th ed., p. 3-71, McGraw-Hill, Inc., 1963.

B. The Volume of the Tubing

The tubing volume between the cell connection (Valve No. 2) and the dead-weight gauge was determined by using nitrogen. The details of the method are given in Section IV.

The volume of the tubing can be calculated by using the following equation:

$$V_t = \frac{Z_1 T_1 P_2}{Z_2 T_2 P_1 - Z_1 T_1 P_2} V_c \qquad \text{(D-1)}$$

where V_t = volume of the tubing

V_c = volume of the cell

P_1 = pressure in the tubing before expansion

P_2 = pressure in the tubing plus the cell after expansion

T_1 = temperature before expansion

T_2 = temperature after expansion

Z_1 = compressibility factor of nitrogen at T_1 and P_1

Z_2 = compressibility factor of nitrogen at T_2 and P_2

The details of the volume measurements may be summarized as follows:

Test No.		Pressure (kPa)	Temperature (K)	Z[**]	Tubing Volume (ml)
1	Initial	6628.7	295.2	0.9979	
	Final	857.29	295.5	1.0378	10.600
2	Initial	5130.7	295.5	0.9978	
	Final	648.11	295.6	1.0126	10.616
3	Initial	9401.1	295.1	1.0062	
	Final	1182.5	295.5	1.0159	10.613

The average volume of the tubing = 10.609 ml

[**] Starling, K.E., "Fluid Thermodynamic Properties for Light Petroleum Systems", p. 187, Gulf Publishing Company, Houston, 1973.

C. <u>Critical Volume of Carbonyl Sulfide</u>

The method of determining the critical volume of carbonyl sulfide (COS) was described in detail in Section IV. Briefly, when the critical point was obtained, the temperature of the cell contents was brought to 323.2 K. Carbonyl sulfide was then expanded into the bomb and tubing system where carbonyl sulfide condensed in the bomb at 273.2 K under the corresponding vapor pressure. Therefore, the amount of carbonyl sulfide collected in the bomb was determined by weighing. The amount of carbonyl sulfide remaining in the equilibrium cell and the tubing was calculated from the known volume, pressure, and temperature using the molal density previously determined at 323.2 K in the Burnett experiments.

The details of the critical volume measurements of carbonyl sulfide are given below:

a - <u>The Amount of COS in the Bomb</u> = 31.737 g

b - <u>The Amount of COS in the Equilibrium Cell and Tubing</u>

$$\text{The cell temperature} = 323.2 \text{ K}$$

$$\text{The cell pressure} = 720.37 \text{ kPa}$$

$$\text{Compressibility factor} = 0.9315$$

The volume of the cell plus tubing = 85.313 ml

∴ The amount of carbonyl sulfide = 1.475 g

c - <u>Critical Volume of Carbonyl Sulfide</u>

The Amount of COS in the Bomb = 31.737 g

The Amount of COS in the cell plus tubing = 1.475 g

∴ The Total Amount of COS at the Critical Point = 33.212 g

∴ The Critical Volume of Carbonyl Sulfide = 0.135 $m^3/kmol$

APPENDIX E

VAPOR PRESSURE DATA OF CARBONYL SULFIDE

Table E-1. Measured Vapor Pressure Data of Carbonyl Sulfide

Temperature (K)	Pressure (kPa)
264.5	496.98
275.6	695.38
283.9	880.68
301.5	1387.1
313.8	1853.4
323.9	2304.1
331.7	2700.9
339.0	3129.2
343.3	3399.4
352.4	4022.9
361.9	4757.1
373.0	5752.6
378.7	6331.7

APPENDIX F

REFRACTIVE INDEX MEASUREMENTS OF CARBONYL SULFIDE

Table F-1. The Refractive Indices and Estimated Densities of Carbonyl
Sulfide at <u>273.2 K</u>

$$R_{LL}^{o} = 0.0141 \ m^3/kmol$$
$$m = 0.646 \times 10^{-5} \ kPa^{-1}$$

| Pressure | Refractive | Index[*] | Density | (kmol/m³) |
(MPa)	Vapor	Liquid	Vapor	Liquid
0.3137	1.0034		0.163	
0.3965	1.0043		0.202	
0.5137	1.0055		0.263	
0.5895	1.0064		0.305	
1.472		1.3785		16.67
2.865		1.3793		16.93
4.161		1.3805		17.20
5.540		1.3823		17.53
7.015		1.3838		17.85
10.46		1.3869		18.64
13.81		1.3894		19.45
17.05		1.3915		20.28
19.94		1.3934		21.07

[*] Values measured relative to vacuum at 6328 Å and presented in
Tables F1 through F-7.

Table F-2.   The Refractive Indices and Estimated Densities of Carbonyl
Sulfide in the Liquid Phase at 288.2 K

$$R_{LL}^{\circ} = 0.0138 \ m^3/kmol$$

$$m \ = -0.562 \times 10^{-5} \ kPa^{-1}$$

Pressure (MPa)	Refractive Index	Density (kmol/m^3)
1.272	1.3608	16.22
2.810	1.3627	16.52
4.133	1.3644	16.78
5.547	1.3660	17.06
6.809	1.3674	17.32
10.22	1.3711	18.03
13.41	1.3744	18.74
16.88	1.3780	19.55
19.88	1.3808	20.29

Table F-3. The Refractive Indices and Estimated Densities of Carbonyl
Sulfide in the Liquid Phase at <u>303.2 K</u>

$$R_{LL}^{\circ} = 0.0136 \text{ m}^3/\text{kmol}$$

$$m = -0.482 \times 10^{-5} \text{ kPa}^{-1}$$

Pressure (MPa)	Refractive Index	Density (kmol/m^3)
1.507	1.3445	15.77
2.796	1.3468	16.02
4.127	1.3490	16.28
5.609	1.3514	16.56
6.616	1.3527	16.75
7.181	1.3533	16.85
9.939	1.3571	17.39
13.60	1.3618	18.13
16.41	1.3649	18.71
19.73	1.3684	19.41
20.52	1.3691	19.58

Table F-4. The Refractive Indices and Estimated Densities of Carbonyl
Sulfide at 323.2 K

$$R_{LL}^{\circ} = 0.0135 \ m^3/kmol$$

$$m = -0.384 \times 10^{-5} \ kPa^{-1}$$

Pressure (MPa)	Refractive Index Vapor	Refractive Index Liquid	Density (kmol/m^3) Vapor	Density (kmol/m^3) Liquid
0.4171	1.0034		0.168	
0.6309	1.0051		0.251	
0.7963	1.0064		0.318	
1.089	1.0092		0.458	
1.296	1.0115		0.569	
1.510	1.0137		0.683	
1.844	1.0175		0.873	
2.065	1.0204		1.016	
2.424		1.3208		14.95
2.899		1.3221		15.04
4.120		1.3249		15.28
5.430		1.3278		15.52
7.016		1.3310		15.82
10.19		1.366		16.39
13.70		1.3422		17.01
17.39		1.3475		17.68
20.35		1.3515		18.22

Table F-5.   The Refractive Indices and Estimated Densities of Carbonyl
Sulfide in the Liquid Phase at 343.2 K

$$R_{LL}^{\circ} = 0.0135 \ m^3/kmol$$

$$m \quad = -0.294 \times 10^{-5} \ kPa^{-1}$$

Pressure (MPa)	Refractive Index	Density (kmol/m³)
3.651	1.2933	13.75
4.175	1.2957	13.89
5.030	1.2990	14.09
5.809	1.3016	14.26
7.057	1.3055	14.51
10.10	1.3138	15.08
13.83	1.3221	15.73
17.10	1.3325	16.45

Table F-6. The Refractive Indices and Estimated Densities of Carbonyl
Sulfide in the Liquid Phase at 363.2 K

$$R_{LL}^{\circ} = 0.0137 \ m^3/kmol$$

$$m = -0.212 \times 10^{-5} \ kPa^{-1}$$

Pressure (MPa)	Refractive Index	Density (kmol/m^3)
5.623	1.2599	12.15
6.885	1.2701	12.64
8.512	1.2794	13.12
9.815	1.2853	13.43
11.02	1.2900	13.69
12.54	1.2953	13.99
13.92	1.2994	14.23
17.32	1.3083	14.79
20.47	1.3149	15.25

Table F-7.   The Refractive Indices and Estimated Densities of Carbonyl
Sulfide at 383.2 K

$$R_{LL}^{o} = 0.0141 \text{ m}^3/\text{kmol}$$

$$m = -0.139 \times 10^{-5} \text{ kPa}^{-1}$$

Pressure (MPa)	Refractive Index	Density (kmol/m^3)
1.665	1.0133	0.632
2.851	1.0235	1.114
4.230	1.0385	1.827
5.602	1.0619	2.932
6.161	1.0791	3.739
8.326	1.2285	10.49
9.767	1.2461	11.29
10.99	1.2563	11.75
12.34	1.2645	12.14
13.85	1.2718	12.49
15.31	1.2781	12.79
18.90	1.2900	13.41

APPENDIX G

PREDICTED PROPERTIES OF CARBONYL SULFIDE

Table G-1. The Molar Volumes and the Compressibility factors of Vapor
Carbonyl Sulfide Predicted by Using BWR
and PR Equations of State

Temperature (K)	Pressure (MPa)	Molar Vol. $(m^3/kmol)$		Compressibility Factor	
		BWR	PR	This Work	PR
273.2	0.18053	12.27	12.25	0.9714	0.9735
"	0.21283	10.36	10.33	0.9649	0.9686
"	0.26354	8.302	8.281	0.9589	0.9609
"	0.30982	7.013	6.992	0.9495	0.9538
"	0.38198	5.626	5.604	0.9398	0.9425
"	0.44708	4.757	4.736	0.9265	0.9322
"	0.54728	3.823	3.801	0.9104	0.9159
"	0.63595	3.240	3.218	0.8911	0.9011
323.2	0.16104	16.46	16.43	0.9855	0.9849
"	0.19671	13.47	13.47	0.9813	0.9816
"	0.23634	11.14	11.12	0.9782	0.9778
"	0.28741	9.120	9.096	0.9724	0.9729
"	0.34593	7.537	7.513	0.9684	0.9673
"	0.41941	6.175	6.151	0.9598	0.9602
"	0.50381	5.101	5.077	0.9539	0.9519
"	0.60839	4.182	4.158	0.9417	0.9415
"	0.72824	3.454	3.429	0.9327	0.9294
"	0.87445	2.834	2.809	0.9155	0.9143
"	1.0407	2.340	2.315	0.9015	0.8968
"	1.2389	1.923	1.898	0.8772	0.8752
"	1.4605	1.589	1.564	0.8557	0.8500
"	1.7154	1.309	1.284	0.8216	0.8196
"	1.9901	1.086	1.059	0.7887	0.7846
"	2.2710	0.909	0.882	0.7357	0.7456

Table G-1. (Continued)

Temperature (K)	Pressure (MPa)	Molar Vol.(m^3/kmol) BWR	PR	Compressibility Factor This Work	PR
383.2	0.21085	14.94	14.92	0.9958	0.9877
"	0.26144	12.02	12.00	0.9868	0.9848
"	0.26678	11.77	11.76	0.9880	0.9845
"	0.29445	10.65	10.63	0.9859	0.9828
"	0.30904	10.14	10.12	0.9874	0.9820
"	0.38268	8.157	8.139	0.9772	0.9776
"	0.38986	8.003	7.985	0.9768	0.9772
"	0.43055	7.231	7.213	0.9753	0.9748
"	0.45019	6.908	6.890	0.9731	0.9736
"	0.55889	5.531	5.513	0.9655	0.9672
"	0.56969	5.423	5.405	0.9656	0.9665
"	0.62731	4.909	4.891	0.9616	0.9631
"	0.65745	4.676	4.658	0.9614	0.9613
"	0.81364	3.745	3.727	0.9509	0.9519
"	0.82719	3.681	3.663	0.9486	0.9510
"	0.91113	3.325	3.307	0.9446	0.9459
"	0.95436	3.166	3.148	0.9441	0.9433
"	1.1751	2.538	2.520	0.9291	0.9297
"	1.1936	2.495	2.478	0.9259	0.9286
"	1.3122	2.253	2.236	0.9204	0.9212
"	1.3738	2.144	2.127	0.9194	0.9173
"	1.665	1.736	1.719	0.8267	0.8988
"	1.6819	1.717	1.700	0.8997	0.8978
"	1.7068	1.689	1.672	0.8958	0.8962
"	1.8709	1.524	1.507	0.8878	0.8855
"	1.9537	1.452	1.435	0.8846	0.8801
"	2.3692	1.162	1.146	0.8574	0.8524
"	2.4025	1.143	1.127	0.8530	0.8502
"	2.6195	1.032	1.015	0.8409	0.8353
"	2.7285	0.9825	0.9664	0.8358	0.8277
"	2.851	0.9312	0.9152	0.8030	0.8190
"	3.2562	0.7881	0.7726	0.7972	0.7897
"	3.2987	0.7750	0.7865	0.7923	0.7596

Table G-1. (Continued)

| Temperature (K)	Pressure (MPa)	Molar Vol. (m^3/kmol) BWR	Molar Vol. (m^3/kmol) PR	Compressibility Factor This Work	Compressibility Factor PR
383.2	3.5666	0.6995	0.6844	0.7746	0.7662
"	3.7029	0.6650	0.6501	0.7673	0.7556
"	4.230	0.5509	0.5368	0.7267	0.7127
"	4.3717	0.5244	0.5106	0.7104	0.7006
"	4.6737	0.4725	0.4592	0.6867	0.6736
"	4.8112	0.4506	0.4376	0.6745	0.6608
"	5.4840	0.3549	0.3433	0.6029	0.5910
"	5.602	0.3395	0.3282	0.5998	0.5771
"	5.7557	0.3197	0.3089	0.5722	0.5581
"	5.8866	0.3030	0.2927	0.5584	0.5408
"	6.161	0.2677	0.2585	0.5172	0.4997
"	6.3591	0.2406	0.2324	0.4730	0.4638
"	6.5152	0.2167	0.2096	0.4382	0.4286
"	6.5899	0.2036	0.1972	0.4229	0.4079
"	6.7783	0.1575	0.1562	0.3411	0.3223
"	6.8242	0.1444	0.1458	0.3105	0.3123
"	6.8628	0.1363	0.1391	0.2980	0.2997
"	7.1192	1.114	0.1194	0.2424	0.2669
"	7.5485	0.1031	0.1078	0.2323	0.2553
"	8.1732	0.09542	0.09951	0.2399	0.2552
"	8.326	0.09415	0.09806	0.2491	0.2562
"	9.767	0.08655	0.08919	0.2717	0.2734
"	10.99	0.08288	0.08472	0.2935	0.2921
"	12.34	0.08002	0.08116	0.3192	0.3143
"	13.85	0.07764	0.07816	0.3482	0.3397
"	15.31	0.07582	0.07587	0.3756	0.3646
"	17.940	0.07329	0.07278	0.4133	0.4092
"	18.90	0.07253	0.07171	0.4427	0.4254
"	32.962	0.06575	0.06339	0.6865	0.6552
"	49.669	0.06165	0.05857	0.9871	0.9128

Table G-2. The Molar Volumes and the Compressibility Factors of Liquid
Carbonyl Sulfide Predicted by Using BWR
and PR Equations of State

Temperature (K)	Pressure (MPa)	Molar Volume 10^2 (m^3/kmol)		Compressibility Factor	
		BWR	PR	This Work	PR
273.2	1.472	5.479	5.347	0.0389	0.03466
"	2.865	5.462	5.321	0.0745	0.06712
"	4.161	5.447	5.298	0.1065	0.09706
"	5.540	5.431	5.275	0.1392	0.1287
"	7.016	5.415	5.251	0.1731	0.1622
"	10.46	5.379	5.200	0.2471	0.2395
"	13.81	5.346	5.155	0.3127	0.3135
"	17.05	5.315	5.116	0.3703	0.3841
"	19.94	5.291	5.083	0.4166	0.4462
288.2	1.272	5.713	5.606	0.03274	0.02977
"	2.810	5.687	5.564	0.07100	0.06525
"	4.133	5.666	5.531	0.1028	0.09542
"	5.547	5.644	5.498	0.1357	0.1273
"	6.809	5.625	5.469	0.1641	0.1554
"	10.22	5.578	5.401	0.2364	0.2303
"	13.41	5.537	5.343	0.2987	0.2990
"	16.88	5.496	5.288	0.3602	0.3725
"	19.88	5.463	5.245	0.4089	0.4352
303.2	1.507	5.983	5.923	0.03791	0.03540
"	2.796	5.951	5.871	0.06925	0.06512
"	4.127	5.921	5.821	0.1006	0.09529
"	5.609	5.889	5.770	0.1344	0.1284
"	6.616	5.874	5.738	0.1495	0.1506
"	7.181	5.857	5.720	0.1691	0.1630
"	9.939	5.805	5.643	0.2267	0.2225

Table G-2. (Continued)

Temperature (K)	Pressure (MPa)	Molar Volume 10^2 (m^3/kmol)		Compressibility Factor	
		BWR	PR	This Work	PR
303.2	13.60	5.742	5.554	0.2976	0.2996
"	16.41	5.699	5.494	0.3480	0.3576
"	19.73	5.651	5.431	0.4032	0.4251
"	20.52	5.641	5.417	0.4156	0.4409
"					
323.2	2.424	6.428	6.475	0.06036	0.05841
"	2.899	6.407	6.438	0.07174	0.06947
"	4.120	6.356	6.350	0.1004	0.09738
"	5.430	6.306	6.267	0.1302	0.1266
"	7.016	6.250	6.170	0.1651	0.1613
"	10.19	6.154	6.031	0.2314	0.2287
"	13.70	6.063	5.899	0.2997	0.3007
"	17.39	5.980	5.784	0.3663	0.3744
"	20.35	5.921	5.706	0.4158	0.4321
343.2	3.651	7.069	7.306	0.09304	0.09348
"	4.175	7.017	7.215	0.1054	0.1056
"	5.030	6.941	7.085	0.1251	0.1249
"	5.809	6.880	6.982	0.1428	0.1422
"	7.057	6.793	6.842	0.1705	0.1692
"	10.10	6.621	6.578	0.2346	0.2328
"	13.83	6.459	6.343	0.3083	0.3076
"	17.10	6.345	6.185	0.3643	0.3707

THE FORMAT

Table G-2. (Continued)

Temperature (K)	Pressure (MPa)	Molar Volume 10^2 (m^3/kmol)		Compressibility Factor	
		BWR	PR	This Work	PR
363.2	5.623	8.081	8.536	0.1533	0.1589
"	6.885	7.763	8.054	0.1804	0.1836
"	8.512	7.494	7.659	0.2149	0.2158
"	9.815	7.334	7.429	0.2421	0.2415
"	11.02	7.213	7.258	0.2666	0.2649
".	12.54	7.085	7.079	0.2968	0.2939
"	13.92	6.985	6.943	0.3238	0.3200
"	17.32	6.787	6.675	0.3878	0.3828
"	20.47	6.642	6.484	0.4445	0.4395

Table G-3. The Vapor Pressure Data of Carbonyl Sulfide Predicted Using
PR Equation of State and the Molar Volumes of Carbonyl Sulfide
Predicted Using BWR and PR Equations of State

Molar Volume 10^2, $(m^3/kmol)$

Temper-ature (K)	Pressure (kPa)		BWR		PR	
	This Work	PR	Liquid	Vapor	Liquid	Vapor
264.5	496.98	498.22	5.369	407.8	5.239	404.7
275.6	695.38	696.99	5.524	296.7	5.400	293.7
283.9	880.68	881.91	5.649	236.6	5.538	233.7
301.5	1387.1	1387.6	5.952	151.5	5.887	148.7
313.8	1853.4	1853.8	6.208	112.7	6.200	109.9
323.9	2304.1	2304.1	6.455	89.58	6.514	86.53
331.7	2700.9	2713.4	6.680	75.25	6.805	72.03
339.0	3129.0	3138.2	6.930	63.48	7.135	60.55
343.3	3399.4	3413.3	7.104	57.52	7.365	54.53
352.4	4022.9	4043.5	7.557	46.45	7.959	43.52
361.9	4757.1	4786.9	8.264	36.60	8.852	33.74
373.0	5752.6	5772.9	10.07	25.92	10.82	23.45
378.7	6331.7	6331.8	19.85	19.86	17.05	17.05